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RECOMMENDED METHODS OF REDUCTION, NEUTRALIZATION, RECOVERY, OR DISPOSAL OF HAZARDOUS WASTE

VOLUME XV. RESEARCH AND DEVELOPMENT PLANS

TRW Systems Group

PREPARED FOR
Environmental Protection Agency

August 1973

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Volume XV. Research and Development Plans

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in:

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

Under Section 212 of Public Law 91-512, the Resource Recovery Act of 1970, the U.S. Environmental Protection Agency is charged with preparing a comprehensive report and plan for the creation of a system of National Disposal Sites for the storage and disposal of hazardous wastes. The overall program is being directed jointly by the Solid and Hazardous Waste Research Laboratory, Office of Research and Development, National Environmental Research Center, Cincinnati, and the Office of Solid Waste Management Programs, Office of Hazardous Materials Control. Section 212 mandates, in part, that recommended methods of reduction, neutralization, recovery, or disposal of the materials be determined. This determination effort has been completed and prepared into this 16-volume study. The 16 volumes consist of profile reports summarizing the definition of adequate waste management and evaluation of waste management practices for over 500 hazardous materials. In addition to summarizing the definition and evaluation efforts, these reports also serve to designate a material as a candidate for a National Disposal Site, if the material meets criteria based on quantity, degree of hazard, and difficulty of disposal. Those materials which are hazardous but not designated as candidates for National Disposal Sites, are then designated as candidates for the industrial or municipal disposal sites.

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This volume of the final report presents more detailed information for some of the projects proposed and summarized in Chapter 6 of Volume I. This volume contains two types of project descriptions: (1) where TRW has had previous experience with a similar project, or (2) where proof-of-principle experimentation has been performed by TRW. Of the projects described herein, proof-of-principle experimentation has been performed for the cementation processes, both inorganic and organic, for the sulfur sequestering, for arsenic removal from soil, and for the recovery of alumina from clay and sulfur oxide scrubbing wastes. The project descriptions are intended to provide further background and technical rationale for the use of the proposed approaches summarized in Volume I.

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CHARACTERIZATION OF INCINERATION PARAMETERS FOR THE SAFE DISPOSAL OF PESTICIDES

1. Introduction

The disposal of pesticide wastes and containers contaminated by pesticide residues is one of the serious environmental problems that has caused growing concern in recent years. Large stocks of surplus pesticide wastes have been accumulated as a result of the cancellation of registrations, the degradation of pesticides from either long-term or improper storage conditions, and the cleaning of empty pesticide containers by rinsing. Conventional means of disposal such as deep-well injection and sanitary landfill without prior detoxification have been deemed inadequate because of potential pollution to land and water. At the present time, TRW has determined that controlled incineration at high temperatures followed by efficiency scrubbing of the furnace gas effluent is the only satisfactory method for the disposal of bulk quantities of organic and metallo-organic pesticide chemicals in concentrated form.

It is recognized that a number of the incinerators currently in use for the disposal of industrial and municipal wastes are readily adaptable to the disposal of pesticide wastes. On the other hand, information on the combustion characteristics of pesticides is limited so that at present it is not possible to identify those existing incinerator installations that could be safely used for the disposal of pesticide wastes. In its investigation under the current contract, TRW has concluded that very little practical experimental data relating to the incineration of pesticides has been determined. In order to fill this gap in the technological base for pesticide disposal, TRW recommends a program to provide the necessary pesticide incineration data by pilot scale testing and to utilize these data for the certification of specific incinerator installations for pesticide disposal. To achieve these objectives in a short period of time, the recommended study is subdivided into the following tasks:

(1) Characterization of pesticide incineration to the degree necessary for incinerator selection.

(2) Development of qualification procedures for incinerators suitable for pesticide disposal.

(3) Identification and testing of incinerator installations throughout the country for safe pesticide disposal.

The approach which TRW proposes is detailed in the following paragraphs.

2. Technical Plan

Characterization of Pesticide Incineration

Determination of Test Parameters. The operational characteristics of currently available incinerator systems would be reviewed and selections made of the nominal ranges of combustion temperature, residence time, and excess air requirements that will be investigated in pilot scale pesticide incineration. The consideration of turbulence will be limited to the assurance that in all cases the turbulence attained in the pilot work will be at least as good as that achievable in the best commercially available incineration units. This approach would serve not only to limit the variable ranges to be examined, but also to ensure that the information generated in the pilot study would be applicable to state-of-the-art equipment.

Incinerator-Scrubber Design and Installation. A pilot scale incinerator would be designed and fabricated. The incinerator would be designed to allow for variable changes over the ranges of interest. It would be instrumented to monitor all variables of importance including effluent pollutant levels. Sampling points would be located along the furnace length so that the effects of residence time could be determined by chemical analysis of the collected samples. It is currently expected that the incinerator furnace design would be similar to that currently employed by TRW for testing injector designs and operating conditions to minimize oxides of nitrogen emissions. The fuel/air injection system would be designed to provide the capability for combusting mixtures over a wide fuel-to-air ratio

including those with excess nitrogen and excess oxygen. Special consideration would be taken in the design to ensure mixing of the fuel and air prior to ignition, and to ensure simulation of a high turbulence commercial incinerator.

A scrubber system would be designed and installed to protect operating personnel and equipment as well as ensure against atmospheric pollution. The scrubber system effluents would be monitored to ensure that acceptable emission levels are maintained. The exact configuration of the scrubber system is of secondary importance to the objectives of the program since the amount of pesticide fed to the incinerator would be regulated to ensure that pollutant loadings (HCl, HF, SO_x, NO_x, P_2O_5, $COCl_2$) in the incinerator effluent were consistent with those currently being efficiently abated with state-of-the-art scrubbing equipment.

Development of Analytical Procedures. The proper evaluation of the incinerator and scrubber system for the safe disposal of pesticides requires the careful sampling and analysis of the feed pesticides, solvent, and auxiliary fuel, the intake air, combustion products along the incineration path, the scrubber liquor, and the stack effluent. In general, the feed gases and liquids would only have to be measured periodically to ensure that the composition of each input component remains relatively constant, whereas the incinerator and scrubber effluents would be closely monitored.

Analysis of the gas samples would be accomplished by the application of both gas chromatography and mass spectrometry. Gas chromatography with electron capture detection would be employed to determine the constituents of the gas samples quantitatively and a mass spectrometer would be used from time to time to qualitatively identify each constituent.

Pesticides and solvent residues and other organic intermediates present in the aqueous scrubber liquor would be extracted with appropriate organic solvents such as hexane, isooctane, and kerosene. Liquid chromatography with UV detectors would be utilized for the quantitative

analysis of the extracted samples, and the liquid fraction collected from the liquid chromatograph detector effluent would be subsequently analyzed in a mass spectrometer for the identification of the chemical species present.

Development of Data Reduction Analysis Program. Data reduction models based on elemental and mass balances would be formulated and programmed for the on-line computer to convert the test data into a useful form. The test information required as input to the program would include the flow rates and chemical composition of the pesticide-solvent, secondary fuel and air fed to the incinerator, the temperature, pressure and gas chromatograph counts for each chemical component in the collected samples along the furnace length and at the stack, and the liquid chromatograph counts for each chemical component in the scrubber liquor. Output information from the program would include the percent of pesticide destroyed and the composition of the effluent gas as functions of residence time and incineration temperature, as well as estimates on the amount of ash obtained.

Selection of Representative Pesticides. Key pesticides representative of the major pesticide families would be selected based on the following criteria: production volume, volume in storage awaiting disposal, toxicity, persistence in the environment, and chemical classification. The latter consideration would also take into account the possible release of harmful combustion products such as hydrogen chloride, hydrogen sulfide, sulfur dioxide, nitrogen and phosphorus oxides. For the pesticides selected, both the reagent grade and the common commercial formulations would be employed in the testing.

Selection of Solvents and Secondary Fuel. Solvents would be selected and purchased for use as a carrier and/or a diluent for the candidate pesticides when the form of the pesticide so requires. The primary considerations in selecting the appropriate solvents would be the hazardous properties of the individual solvents, the solvent cost per unit weight of pesticide dissolved, as well as the additional use of the solvent as a fuel.

If necessary, a secondary fuel would be selected for use in the incinerator as both a heat source and a hydrogen source to ensure that any halogen gases formed during combustion are converted to hydrogen halides. Elimination of the halogen gases will facilitate more efficient scrubbing of the incinerator effluent as the hydrogen halides are more readily soluble in both aqueous and alkaline solutions.

Selection of Test Conditions and Running of Tests. Test conditions selected would be primarily based on operating conditions found in state-of-the-art incineration technology. Within those operating limits, temperature is the main variable of concern. Higher temperatures lead to the complete combustion of pesticide wastes, but at the same time also favor the formation of halogen gases and nitrogen oxides. On the other hand, too low a temperature results in the release of unreacted pesticides to the atmosphere. To bracket the optimum temperature range for the combustion of a pesticide waste, the upper temperature limit would be determined by examination of the equilibrium combustion product distribution predicted by computerized equilibrium calculations such as the TRW Chemical Analysis Program, whereas the lower temperature limit would be provided by the knowledge that complete combustion of pesticides is usually not obtained below 1,300 F even at very long residence times.

For each pesticide under investigation, a matrix of tests would be performed by varying the combustion mixture of pesticide, solvent, air nitrogen and fuel. Each series of tests would be planned by analyzing the results from previous test runs to ensure that the additional information obtained will always provide useful data points.

Analysis and Presentation of Test Results. Results from the incinerator test runs would be carefully analyzed so that the effects of temperature, residence time, air-to-fuel ratio and type of solvent on the combustion products can each be individually assessed to allow for the determination of the optimum operating conditions for the safe disposal of pesticide wastes.

Development of Qualification Procedures

Determination of Applicable Types of Incinerators. The operational characteristics of the various classes of incinerators would be evaluated to determine which types are applicable to pesticide incineration. The operational characteristics would be determined through contacts with manufacturers and users, as well as a review of current literature including the incineration process reports presented in Volume III.

Determination of Applicable Pesticide and Pesticide Incinerator Product Monitors and/or Analytical Procedures. Applicability of monitoring and analytical instrumentation for full scale pesticide incinerator testing would be determined by the following factors: mobility, precision and accuracy within an acceptable range of error, and ease of operation and maintenance.

Selection of Test Pesticides. The original selection criteria for pesticides employed in pilot scale testing and the test results for these pesticides would be reviewed. Five to ten pesticides requiring more severe operating conditions to attain complete combustion would be selected for testing in the full scale incinerator installations.

Specification of Solvents and Mix Compositions. Based on the results of pilot scale testing, solvent types and solvent/pesticide active ingredient ratios that would bring about the desirable combustion characteristics would be specified.

Recommendation of Effluent Standards. Criteria for permissible levels in public water supplies and in air have already been established for a number of pesticides and related chemical species. For the other pesticides suitable for disposal by incineration, effluent standards would be recommended based on published toxicity data such as the ACGIH TLV's and the 48-hour TL_m for marine organisms. The provisional recommendation developed as a part of the current program, could be used as the effluent standards where other data are not available.

Specification of Operating Ranges. The major factors affecting the incinerator operation are control of temperature, degree of turbulence, and residence time. However, turbulence is difficult to characterize and only the temperature and residence time ranges required to obtain complete combustion of the pesticides would be specified, based on pilot scale test results. As discussed previously, the full scale incinerators normally do not have turbulence characteristics as good as the pilot scale unit used in testing, and hence only those incinerator installations that could meet the temperature and time specifications would be considered for certification testing.

Identification and Certification Testing of Incineration Installations

Survey Manufacturers to Appraise Applicability of Specific Models. The major manufacturers of incineration units would be contacted to determine the applicability of specific units to pesticide incineration. Primary concern would be placed on assuring that proper operational conditions, as determined in the pilot study, can be maintained in the various specific units. A further effort would be made to obtain information which will lead to the generation of a list of owners and/or operators of the specific types of incinerators of interest.

Survey of Organizations Possessing Incinerators. The organizations known to possess and/or operate incinerators which can serve as waste pesticide destructors would be contacted to determine their willingness to be tested, certified and utilized as waste pesticide disposal units. This information would lead to the generation of a list of companies and facilities willing to operate as disposers, as well as any conditions or limitations which those companies feel must be satisfied.

Verification Testing and Issuance of Certifications. Verification tests would be performed including sampling and analysis of waste effluents. Results of the verification tests along with recommendations would be submitted to EPA for final approval and the issuance of certifications.

3. Program Implementation

It is anticipated that the recommended program could be accomplished within a time frame of 12 months at a cost of approximately $250,000. when the optional task of verification testing and issuance of certifications is not included. The manpower required has been estimated to be 7,000 hours of engineering and 3,500 hours of technical support.

NEW CHEMICAL CONCEPTS FOR UTILIZATION OF WASTE PESTICIDES

1. Introduction

The objective of the recommended program "Characterization of Incineration Parameters for the Safe Disposal of Pesticides" is to solve the near term problem of pesticide waste disposal. To obtain more in-depth information on the combustion characteristics of pesticide incineration, the effects of combustible pesticide containers on pesticide incineration, and the possibility of recovering marketable products from the high temperature reactions of pesticides with various reagents, TRW proposes an analytical investigation aimed at: (1) developing thermochemical and kinetic models of the behavior of a broad range of representative pesticides in high temperature combustion and/or coreactant environments; (2) identifying waste pesticide/coreactant products of potential commercial value; and (3) providing preliminary engineering and economic evaluation of processing approaches for waste pesticide utilization. The coreactants would be selected on the basis of cost, availability, and reactivity with the selected pesticides. Since increasing volumes of pesticides are now packaged in plastic containers and containers with plastic liners, the coreactants selected will necessarily include the three most common plastics; polyethylene, polystyrene, and polyvinyl chloride. The knowledge of waste plastics utilization systems acquired from previous investigations such as the TRW study "New Chemical Concepts for Utilization of Waste Plastics" (HEW Bureau of Solid Waste Management Contract PH 86-68-206) could thus be used to provide a strong base for the proposed program.

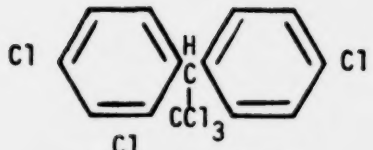
Specifically, TRW recommends a two-part theoretical study program on five representative volume pesticides from the five major pesticide families: DDT (chlorinated hydrocarbons), aldrin (cyclodienes), carbaryl (carbamates), parathion (phosphorus based), and 2,4-D-acid (herbicide). The first task of the program is to determine the equilibrium reaction

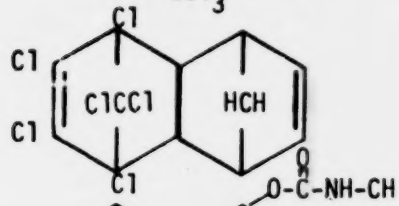
product distributions of the selected pesticide/coreactant systems under a wide range of mixture ratio, temperature, and pressure conditions utilizing an equilibrium calculation program. The results of the thermochemical equilibrium analysis will be examined for commercially attractive end products and potentially harmful pollutants, and would be used to identify the thermochemically feasible reaction paths. The second task of the proposed program is to develop reaction kinetic models suitable for the description of time-dependent behavior of various reactions occurring in pesticide/coreactant systems of interest. The mathematical models would be formulated into computer programs and applied to simulate actual operating conditions. The data generated from the technical analysis would be used to perform preliminary design and economic analysis of chosen chemical processes and provide information on the economic feasibility of waste pesticide and pesticide container utilization methods.

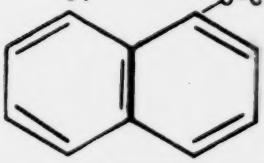
Assuming that safe, economically attractive waste pesticide/coreactant products and processing conditions can be identified, two possible types of reactor hardware systems are currently envisioned. The first system would involve a relatively small, mobile processing unit which could be moved directly to a location of storage of waste pesticides, process those pesticides and then move on to the next storage site. The second approach would involve processing waste pesticides as an intermediate feed along with a continuous feed of waste plastics in a large fixed location plant.

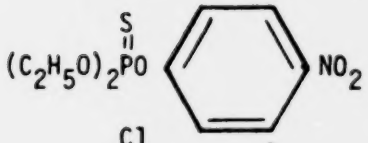
2. Technical Plan

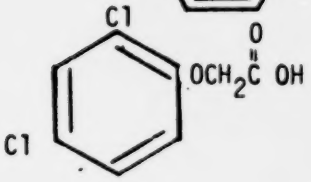
Five volume pesticides epresentative of the major familes of pesticides will be investigated in the program. These are:

(1)  DDT

(2)  ALDRIN

(3)  CARBARYL

(4)  PARATHION

(5)  2,4-D

The primary effort in the program will involve technical and economic evaluation of the chemical interactions of these five pesticides with selected coreactants. This study will involve two interrelated tasks as shown in the project flow diagram (Figure 1) and described below:

Thermochemical Equilibrium Analysis

The objectives of this task are twofold:

(1) To determine the equilibrium product distribution of waste pesticide/coreactant reactions and identify the potential pollutants and marketable products.

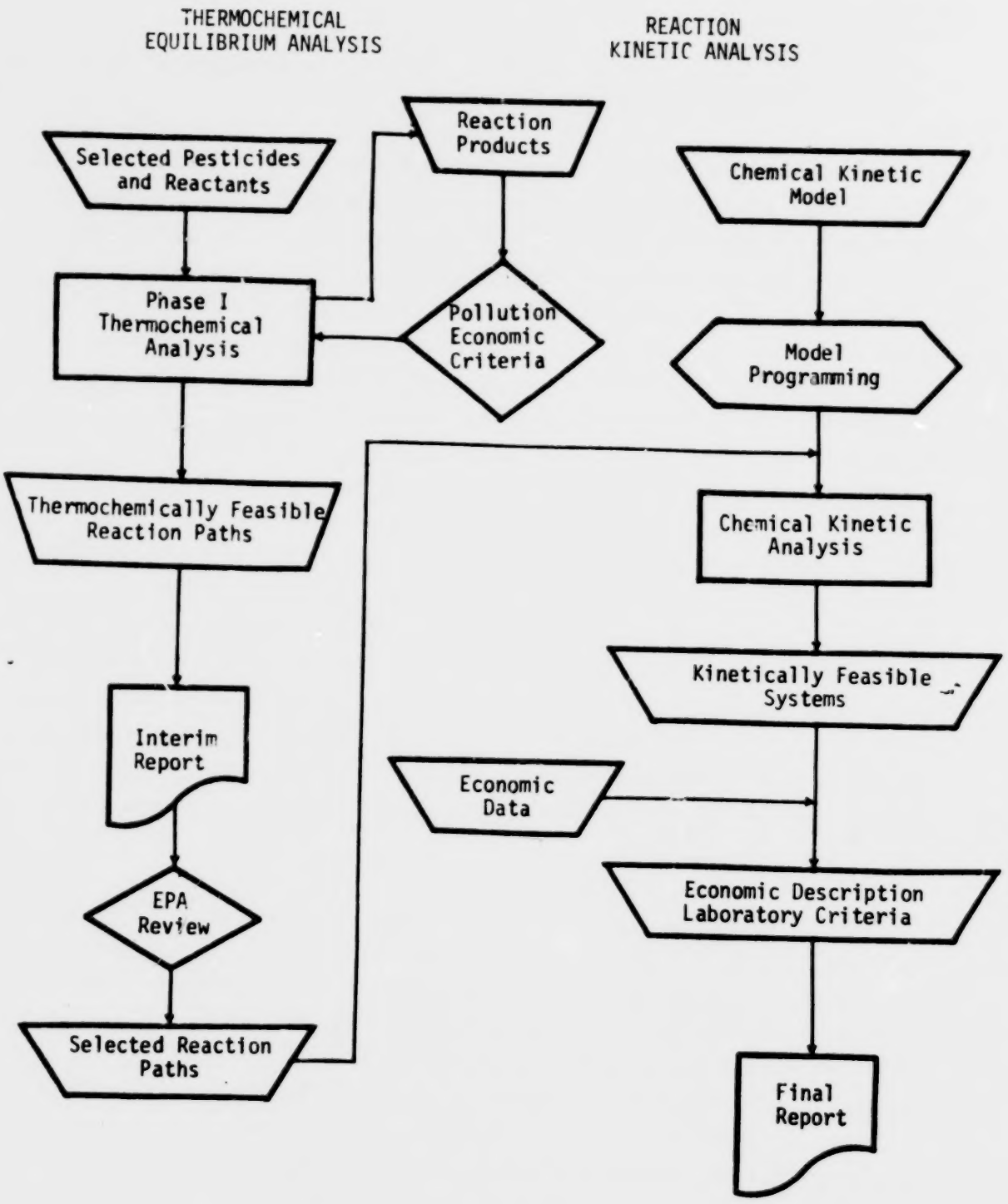


Figure 1. Project Flow Diagram

(2) To determine the thermodynamically feasible reaction paths from pesticide/coreactant reactions to desirable intermediate and/or end products.

The equilibrium product distribution as a function of a broad range of temperature, pressure, and initial reactant composition will be computed rapidly and inexpensively using a computerized equilibrium calculation program such as the TRW developed Chemical Analysis Program. The TRW program is capable of describing systems containing gases, pure liquids, pure solids, and solutions, and simultaneously considering up to 200 gaseous products, together with 50 condensed species. Chemical reagents to react with the five representative pesticides will include air (combustion), steam, polyethylene*, polystyrene*, polyvinyl chloride*, and others to be selected on the basis of cost, availability and reactivity with the pesticides. As an example, the equilibrium product distributions resulting from the thermal decomposition and combustion of each of the five pesticide systems at atmospheric pressure and three temperatures, 1,200 C, 800 C, 500 C have been computed. The numerical results are summarized in the appendix. It is interesting to note that very similar product distributions occur in approximately the same temperature and fuel/air mixture ratio range in the combustion of waste plastics. Thus reactor equipment designed for the partial or total combustion of plastic materials with recovery of products such as HCl would also appear to be suitable for the disposal of plastic pesticide containers.

The thermochemical data base utilized in this example analysis has not been expanded beyond those species required for the waste plastics analysis even though it is clear that the base will require some expansion. Decomposition species determined in the Foster D. Snell, Mississippi State, and Oregon State studies, including the pesticides themselves, which are not currently considered will be added to the data file along with others which appear feasible. Literature information, where available, will be used to prepare the necessary enthalpy and entropy data. Estimation techniques will be used where data are not available.

* Utilization of plastic containers contaminated by pesticide wastes.

The second part of this task involves the application of the thermochemical equilibrium program to determine the thermodynamically feasible reaction paths, i.e., whether or not certain intermediate reaction steps are likely to occur thermodynamically. This will be done simply by rerunning the equilibrium program after deletion of all major equilibrium product species found in the previous run. For example, the DDT thermal decomposition system predicted methane, hydrogen, hydrogen chloride/and graphite as the principal equilibrium products. The first stage of the reaction path analysis will eliminate these species from consideration and perhaps find ethylene, acetylene, methyl chloride, and chlorine to be the next most feasible intermediates. Subsequent deletions will lead to identification of still higher (and probably more valuable) intermediates and a complete description of the possible reaction paths to the thermodynamically stable end products. The resulting information from the reaction path analysis will be used to scope reaction of intermediates and mechanisms for the reaction kinetic model.

Reaction Kinetic Analysis

The second task of the theoretical study will employ mathematical models to describe the time-dependent behavior of pesticide/coreactant reaction systems. Emphasis of the analysis will be placed on the quantitative characterization of reaction products as a function of time and temperature, and the identification of reaction systems leading to the development of economically attractive waste pesticide and pesticide container utilization processes.

The first part of this task will be mathematical modeling of the chemical kinetics of selected pesticide/coreactant reactions in the form of systems of differential equations. Information from the Thermochemical Equilibrium Analysis and the literature will be used to define the reaction intermediates and the decomposition mechanism yielding the identified final products. The reaction rate parameters will be taken from the literature, or estimated by theoretical-empirical techniques when data are not available.

The second part of the Reaction Kinetic Analysis will involve the application of the reaction kinetic models to determine the effects of temperature, pressure, and residence time variation on the product distribution in a kinetically controlled environment. The information obtained will be used in the preliminary design of chemical reactors and processing systems capable of attaining desirable end products.

Finally, the processing concepts for utilization of waste pesticides and pesticide containers will be assessed in terms of their economic potential. The results of the analyses will indicate the direction for future laboratory research on waste pesticides.

3. Program Implementation

It is anticipated that the proposed program could be accomplished within a time frame of 10 to 12 months at a cost of approximately $150,000.

4. Appendix A - Equilibrium Product Distribution

The equilibrium product distribution for the thermal decomposition and air combustion of five selected pesticides as a function of temperature and initial composition* (weight percent pesticides in the reacting system) are presented in this appendix (Tables 1-5). The data format used in the tables is an exponential form, i.e., X.XX-Y is equivalent to X.XX 10^{-Y}. Mole fractions less than 10^{-4} are indicated by - .

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* The case of 100 weight percent pesticide is equivalent to thermal decomposition in an inert atmosphere.

TABLE 1

EQUILIBRIUM COMPOSITION OF DDT/AIR SYSTEM*† (1 ATM PRESSURE) MOLE FRACTION, GAS PHASE

Wt. % Pesticide	Temp.	CH_4	CO	CO_2	H_2	H_2O	HCl	HCN	N_2	Condensed Phase Graphite Mol/100G Feed
100	1200 C	2.331-4	-	-	2.853-1	-	7.144-1	-	-	1.706
	800 C	3.617-3	-	-	2.795-1	-	7.169-1	-	-	1.696
	500 C	6.596-2	-	-	1.726-1	-	7.614-1	-	-	1.522
70	1200 C	1.000-4	1.205-1	-	1.867-1	-	4.678-1	2.673-4	2.246-1	0.840
	800 C	1.541-3	1.148-1	1.880-3	1.824-1	2.736-3	4.706-1	-	2.260-1	0.851
	500 C	2.372-2	1.143-2	3.275-2	1.035-1	5.733-2	5.210-1	-	2.502-1	1.039
50	1200 C	-	2.039-1	-	1.185-1	-	2.969-1	2.771-4	3.802-1	0.119
	800 C	6.191-4	1.924-1	5.280-3	1.156-1	2.907.3	2.995-1	-	3.837-1	0.147
	500 C	8.854-3	1.790-2	8.033-2	6.325-2	5.486-2	3.397-1	-	4.351-1	0.517
20	1200 C	-	-	1.040-1	-	5.514-2	1.236-1	-	6.656-1	-
	800 C	-	-	1.044-1	-	6.129-2	1.123-1	-	6.688-1	-
	500 C	-	-	1.055-1	-	8.321-2	7.096-2	-	6.757-1	-

*The data format used is an exponential form, i.e., X.XX-Y is equivalent to $X.XX\ 10^{-Y}$.

†Mole fractions less than 10^{-4} are indicated by -.

TABLE 2

EQUILIBRIUM COMPOSITION OF PARATHION/AIR SYSTEM (1 ATM PRESSURE) MOLE FRACTION, GAS PHASE*†‡

Wt. % Pesticide	Temp.	CH_4	CO	CO_2	H_2	H_2O	HCN	H_2S	N_2	P_4O_6	Condensed Phase Graphite Mol/100 G Feed
100	1200 C	6.584-4	3.784-1	1.229-4	4.795-1	3.834-4	1.572-4	5.140-2	3.025-2	-	1.693
	800 C	1.224-2	2.812-1	1.129-2	5.142-1	1.890-2	-	9.095-2	4.631-2	2.316-2	2.298
	500 C	1.460-1	1.983-2	9.855-2	2.568-1	2.467-1	-	1.322-1	6.622-2	3.314-2	2.748
70	1200 C	3.384-4	3.693-1	1.171-4	3.438-1	2.683-4	3.417-4	3.538-2	1.993-1	-	0.740
	800 C	5.736-3	2.937-1	1.230-2	3.520-1	1.351-2	-	6.082-2	2.446.1	1.564-2	1.199
	500 C	6.884-2	2.170-2	1.181-1	1.764-1	1.854-1	-	8.288-2	3.254-1	2.081-2	1.800
50	1200 C	1.795-4	3.632-1	1.132-4	2.504-1	1.921-4	3.700-4	2.424-2	3.208-1	-	0.105
	800 C	2.854-3	3.020-1	1.301-2	2.483-1	9.799-3	-	4.195-2	3.695-1	1.092-2	0.461
	500 C	3.465-2	2.319-2	1.347-1	1.251-1	1.405-1	-	5.545-2	4.719-1	1.395-2	1.123
20	1200 C	-	8.885-2	1.109-1	3.222-2	9.896-2	-	9.140-3	6.484-1	5.013-3	-
	800 C	-	6.655-2	1.342-1	4.287-2	7.917-2	-	1.913-2	6.521-1	5.042-3	-
	500 C	5.524-3	2.581-2	1.669-1	4.996-2	6.245-2	-	2.017-2	6.637-1	5.132-3	0.022

*Small amounts of CS_2, COS, P_2, P_4, and S_2 are also present at 1,200 C.

†The data format used is an exponential form, i.e., X.XX-Y is equivalent to X.XX 10^{-Y}.

‡Mole fractions less than 10^{-4} are indicated by -.

TABLE 3

EQUILIBRIUM COMPOSITION OF ALDRIN/AIR SYSTEM (1 ATM PRESSURE) MOLE FRACTION, GAS PHASE*†

Wt. % Pesticide	Temp,	CH_4	CO	CO_2	H_2	H_2O	HCl	HCN	N_2	Condensed Phase Graphite Mol/100 G Feed
100	1200 C	-	-	-	1.428-1	-	8.572-1	-	-	3.288
	800 C	9.222-4	-	-	1.411-1	-	8.579-1	-	-	3.286
	500 C	2.256-2	-	-	1.010-1	-	8.765-1	-	-	3.246
70	1200 C	-	1.573.1	-	7.831-2	-	4.708-1	1.978-4	2.933-1	1.991
	800 C	2.730-4	1.502-1	3.220-3	7.679-2	1.508-3	4.731-1	-	2.948-1	2.003
	500 C	4.302-3	1.572-2	6.191-2	4.409-2	3.357-2	5.178-1	-	3.226-1	2.202
50	1200 C	-	2.396-1	-	4.468-2	-	2.688-1	1.844-4	4.467-1	0.911
	800 C	-	2.259-1	7.280-3	4.371-2	1.291-3	2.711-1	-	4.506-1	0.937
	500 C	1.262-3	2.129-2	1.136-1	2.388-2	2.463-2	3.063-1	-	5.090-1	1.279
20	1200 C	-	5.878-2	1.450-1	2.403-3	1.459-2	1.019-1	-	6.773-1	-
	800 C	-	5.619-2	1.476-1	4.986-3	1.200-2	1.019-1	-	6.773.1	-
	500 C	1.260-4	2.579-2	1.667-1	7.545-3	9.426-3	1.034-1	-	6.871-1	0.045

*The data format used is an exponential form, i.e., X.XX-Y is equivalent to $X.XX\ 10^{-Y}$.

†Mole fractions less than 10^{-4} are indicated by -.

TABLE 4

EQUILIBRIUM COMPOSITION OF 2,4D/AIR SYSTEM (1 ATM PRESSURE) MOLE FRACTION, GAS PHASE*†

Wt. % Pesticide	Temp.	CH_4	CO	CO_2	H	H_2O	HCl	HCN	N_2	Condensed Phase Graphite Mol/100 G Feed
100	1200 C	2.329-4	4.283-1	1.574-4	2.852-1	2.580-4	2.859-1	-	-	2.575
	800 C	3.522-3	3.883-1	2.151-2	2.758-1	1.400-2	2.967-1		-	2.667
	500 C	4.171-2	2.812-2	1.982-1	1.373-1	1.870-1	4.077-1	-	-	3.297
70	1200 C	1.002-4	4.010-1	1.380-4	1.870-1	1.585-4	1.875-1	2.671-4	2.238-1	1.472
	800 C	1.520-3	3.661-1	1.912-2	1.812-1	8.671-3	1.930-1	-	2.304-1	1.558
	500 C	1.832-2	2.772-2	1.925-1	9.099-2	1.222-1	2.499-1	-	2.983-1	2.213
50	1200 C	-	3.820-1	1.253-4	1.189-1	1.000-4	1.192-1	2.772-4	3.794-1	0.554
	800 C	6.167-4	3.508-1	1.756-2	1.154-1	5.292-3	1.220-1	-	3.883-1	0.633
	500 C	7.594-3	2.762-2	1.911-1	5.858-2	7.836-2	1.522-1	-	4.845-1	1.293
20	1200 C	-	7.792-2	1.560-1	8.168-3	4.322-2	5.198-2	-	6.621-1	-
	800 C	-	7.012-2	1.638-1	1.656-2	3.543-2	5.199-2	-	6.621-1	-
	500 C	1.045-3	2.771-2	1.924-1	2.173-2	2.916-2	5.300-2	-	6.750-1	0.056

*The data format used is an exponential form, i.e., X.XX-Y is equivalent to $X.XX\ 10^{-Y}$.

†Mole fractions less than 10^{-4} are indicated by -.

TABLE 5

EQUILIBRIUM COMPOSITION OF CARBARYL/AIR SYSTEM (1 ATM PRESSURE) MOLE FRACTION, GAS PHASE*†

Wt. % Pesticide	Temp.	CH_4	CO	CO_2	H_2	H_2O	HCN	N_2	Condensed Phase Graphite Mol/100 G Feed
100	1200 C	1.346-3	2.500-1	-	6.855-1	3.620-4	2.701-4	6.247-2	4.965
	800 C	2.016-2	2.274-1	7.380-3	6.599-1	1.961-2	-	6.542-2	4.995
	500 C	2.433-1	1.562-2	6.118-2	3.316-1	2.509-1	-	9.711-2	5.145
70	1200 C	6.378-4	2.808-1	-	4.720-1	2.800-4	4.446-4	2.458-1	3.036
	800 C	9.584-3	2.565-1	9.387-3	4.550-1	1.525-2	-	2.542-1	3.098
	500 C	1.158-1	1.850-2	8.582-2	2.288-1	2.051-1	-	3.451-1	3.542
50	1200 C	3.185-4	3.008-1	-	3.335-1	2.119-4	4.552-4	3.647-1	1.750
	800 C	4.807-3	2.758-1	1.086-2	3.222-1	1.162-2	-	3.746-1	1.822
	500 C	5.887-2	2.075-2	1.079-1	1.631-1	1.639-1	-	4.853-1	2.406
20	1200 C	-	2.778-1	2.229-2	1.148-1	2.269-2	-	5.624-1	-
	800 C	2.285-4	2.682-1	3.180-2	1.237-1	1.343-2	-	5.627-1	-
	500 C	9.531-3	2.473-2	1.533-1	6.562-2	7.862-2	-	6.682-1	0.565

*The data format used is an exponential form, i.e., X.XX-Y is equivalent to $X.XX\ 10^{-Y}$.

†Mole fractions less than 10^{-4} are indicated by -.

DEVELOPMENT OF LOW COST CEMENTATION APPROACHES TO PASSIFICATION OF HEAVY METAL SLUDGES AND SOLIDS

The following two research plans describe two different approaches to the stabilization of heavy metal wastes prior to ultimate disposal. The first plan concentrates on agglomerating and solidifying waste sludges with low cost inorganic cements. The second plan involves incorporating a very high loading >90 percent of dry, heavy metal waste into a polymeric matrix. The initial condition of the waste material (sludge or dry solid for example) is likely to determine the most cost effective approach for any particular waste stream.

STABILIZATION OF NONDEGRADABLE TOXIC WASTES BY INORGANIC CEMENTATION

1. Problem Background

Sludges from industrial processing, mineral ore processing, backwash from granular media filters, metallurgical processes, petroleum refining, treatment of municipal sewages, etc., very often contain toxic metal compounds, such as arsenic, mercury, lead, selenium, beryllium, cadmium, zinc, chromium, etc. These hazardous heavy metal compounds represent a danger of reentering into the environment and must be made inert to dispersion before ultimate disposal of the sludge solids. Hazardous sludge solids should be properly inactivated to make them physically and chemically resistant to the action of environmental conditions and properly disposed of in landfills, oceans, backfill mines, otherwise they may reappear in the ecology, e.g. water, air, soil, plants, etc., after a relatively short time. Conversion into a safe and stable form or state from which dissipation into the ecology either does not occur at all or is negligible should precede disposal. The problem of establishing the admissible limits of rate of dissipation for numerous toxic metals and metal compounds is still an open question. As a baseline for evaluating stabilization techniques it is recommended that the rate of dissipation of hazardous metals from their natural ores and at natural conditions (i.e. conditions before any mining operations) be considered the maximum allowable dispersion rate. The problem of safe disposal of hazardous metals and/or their compounds contained in sludges, slurries, solid wates, etc. consists of finding economical method(s) of bringing them into a passive form or passive state or embedding into a passive impermeable matrix.

2. Recommended Technical Approach

It is assumed that the toxic solids subject to stabilization and ultimate disposal do not present any current or future commercial interest

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for recovery and recycling of the metals or their compounds. Technological processes for stabilization of hazardous solids from sludges, slurries, wastes, tailings, etc., must meet certain requirements. The most important are:

(1) the processes must be effective, i.e. the stabilized toxic solids may not reenter into the ecology at a rate greater than the admissible limit;

(2) the process must be economical, its cost will burden the main product(s) responsible for the generation of the sludge or solid wastes; and

(3) Economical considerations impose restrictions of using only the lowest cost materials and reagents and the simplest operations and equipment in processing.

Several processes have been suggested for stabilization of toxic metals and/or their compounds in sludges, slurries, solid wastes, etc., such as caging, encapsulation, complexing, compacting, chelating and cementation*.[1,2] The latter, i.e. cementation shows considerable promise of assuring satisfactory performance combined with potentially low cost. Stabilization of the toxic solids from sludges and wastes by inorganic cementation involves blending and overlaying the sludge solids after proper preparation† with cementitious materials or cement forming raw materials. Setting and hardening of the entire mix follows with a resulting "sludge-concrete". The intended procedure partially resembles cementation or stabilization of soil[3,4] and partially resembles building concretes[5] with the compacted sludge or solid waste replacing, respectively, the soil or sand/rock aggregates. Either inorganic or organic bonding agents or their combinations may be applied.

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*Cementation is taken to include both inorganic and polymeric cements. This research work concentrates primarily on inorganic cements while the one which follows involves polymeric cements.

†Preparation of the solids for cementation from sludges, slurries, and wastes is discussed in the section titled "Technical Problems in Cementation of the Sludges."

Inorganic cements meant for application in the stabilization of sludges are materials which, when mixed with water, form plastic and viscous pastes with bonding properties which set and harden in air or under water. Lime, plaster of paris, portland cement, and calcium aluminate cements belong to this category. Cement forming mixtures are composed of materials which separately may or may not exhibit cementitious properties, but they mutually react with formation of compounds which will set and harden. Examples of such mixtures are lime-clay, lime-pozzolan, calcium aluminate-calcium sulfate, etc.

Bituminous materials, coal tar, coal pitch and asphalts may be attractive as bonding materials for sludge conglomerates both from the point of view of performance as well as cost. The deleterious effect of soil bacteria and fungi may be overcome by incorporating fungitoxic and bacteriatoxic agents. This precaution may be of particular importance if the "sludge-concrete" has to be disposed of in moist and warm sites.

The set, hardened and eventually cured "sludge-concrete" blocks, when removed from wooden rectangle molds are expected to possess sufficient strength for further handling and transportation to the ultimate disposal site. They may or may not exhibit sufficient resistance to land or sea water leaching or to erosion. In the latter case additional surface coating and/or surface hardening may be necessary. Spraying of cemented blocks with metal fluorosilicates (Mg, Zn) may harden the surfaces and increase the resistance to erosion and leaching, and impregnating or coating with bitumens, paraffins, or resins may increase the resistance to leachability.

Economic reasons dictate that the formation of the "sludge-concrete" must be achieved with no more cement than usually used in normal concretes or in cemented soils.

A cement/sludge ratio (on a dry weight base) in excess of 1:5 will probably be prohibitive costwise. While the requirements regarding leachability and erosion resistance are high, the strength requirements are

limited to about 1/10 of the strength of usual concrete compositions. Compressive strength of the "sludge-concrete" of the order of 500 psi will probably be adequate for transportation. The low strength requirements of "sludge-concretes" opens the possibility of substituting for the well-established commercial cements (e.g., portland cement) inferior quality but potentially lower cost cementitious mixtures.

Figure 1 presents a tentative flow diagram of a few alternate procedures for cementation of sludges.

3. Technical Problems in Cementation of Sludges

Characteristics of the Sludges. Sludges have to be distinguished from slurries. Slurries are liquids having sufficient suspended solids to be a distinct phase. The solids in slurries are usually granular or crystalline, but sometimes may be amorphous. Sludges are thick viscous mixtures of solids and liquids, in appearance they resemble a single phase and generally have little, if any, free liquid. These semi-liquid wastes have a total solids concentration of at least 2,500 ppm. They are obtained from waste water containing impurities by processes, such as liquid-solid separation (e.g., sedimentation, clarification), a chemical reaction, e.g. coagulation, or a biological process. Often they are jelly-like and colloidal with a gray, black, brown or other color. Usually sludges can be made to flow, can be pumped, and exhibit thixotropic properties. In most cases they are too liquid for transportation by a conveyor or shovel. Sludges vary in moisture content from 99 percent, which is typical for alum sludges from water treatment plants, to perhaps 40 to 50 percent which is typical for chemical plant sludges, clay products, evaporated black liquor wastes in pulp and paper mills. The characteristics of a sludge depend on the quantity and type of suspended and dissolved materials. Sludges contain water in at least four different ways:

(1) chemically combined water, such as the water of hydration;

(2) colloidally held or "bound" water;

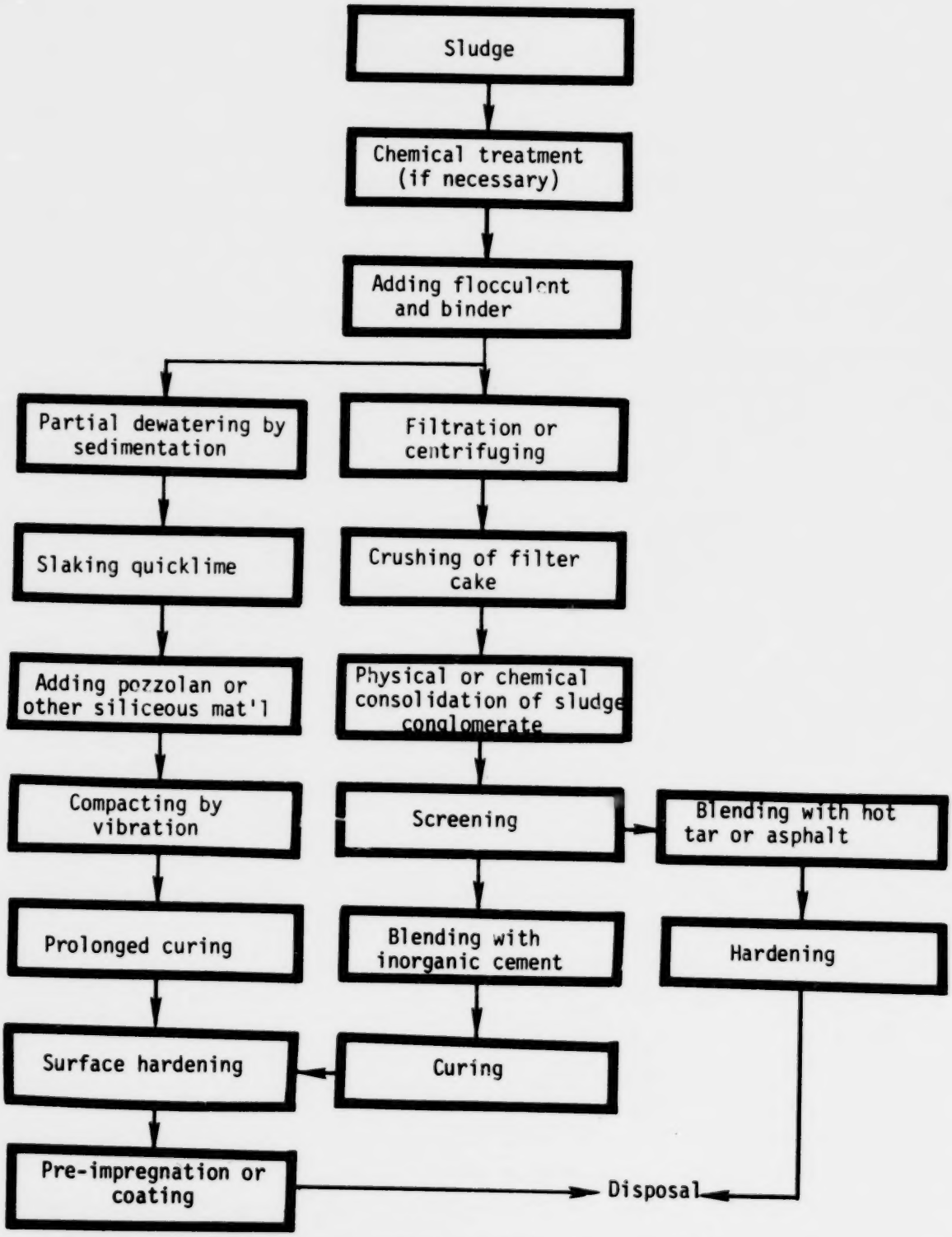


Figure 1. Stabilization of hazardous sludges by cementation

(3) physically trapped or confined water (such as inside living cell walls or in hollow fibers);

(4) water of dilution or entrained water.

Most sludges are aqueous, but there are also sludges based on alcohols, ethers, or other liquids that are used in chemical processing. Sludges are difficult to dewater, transport, or keep from emitting odors. Treatment of sludges depends on their settleability, filterability, pH, turbility, biodegradability, odor, etc.

Preparation of the Sludge for Inorganic Cementation. The preparation of the sludge for cementation may include the following operations:

(1) Total removal or at least maximal reduction of toxic ions from surrounding solution.

(2) If necessary or practical converting the sludge solids into compounds having minimum solubility and which do not interfere in setting or hardening of the applied cement.

(3) Dewatering of the sludge.

(4) Consolidation of the sludge solids into a conglomerate suitable for cementation.

Removal or maximum reduction of the concentration of toxic ions in solution surrounding the sludge aims at achieving practically toxic-ion-free solution after subsequent total or partial dewatering of the sludge. This may be achieved by adding an excess of the precipitating ions at selected pH and temperature. The latter being controlled because the solubility product is pH and temperature dependent. For example, if calcium arsenate is the toxic component of the sludge, the concentration of AsO_4^{-3} ions may be reduced by an excess of Ca^{++} ions, and if HgS is the toxic compound, an excess of S^{--} ions will be necessary.

Conversion of sludge toxic solids into other compounds may be necessary in two cases: if the solubility of the toxic compound is too high and if following the separation of solids the remaining solution still contains an excessive amount of toxic ions which cannot be otherwise economically removed; of if the toxic solid is harmful for setting or curing of the "sludge concrete" (see additives to cement in the next paragraph).

For example, cadmium and zinc hydroxides are known to inhibit setting of cements. Converting these solids into silicates ($ZnSiO_3$ or Zn_2SiO_4 and $CdSiO_3$ or Cd_2SiO_4) with SiO_3^{2-} or SiO_4^{4-} anions respectively (addition of water glass) or into fluorosilicates $ZnSiF_6$ and $CdSiF_6$ may solve the problem.

Dewatering of the sludge. Most sludges contain more water than may be needed in cement-sludge-conglomerate-water mixtures in making "sludge concrete". Apart from this, it is doubtful if chemically or colloidally-bound water from sludges may be useful for hydration of hydraulic cements. The removal of unwanted kinds and excess of water may be economically achieved by flocculating the sludge solid particles with either inorganic or organic flocculents or mixtures of both, followed by sedimentation, vacuum filtration, or centrifuging. Flocculents which may contribute to the consolidation of the sludge solids and act as binders should be preferred. Among flocculents and binders worthy of consideration are: limes, alums, veegum (hydrated magnesium silicates), clays, acrylamides, stearine and sterates, gum arabic, polyvinyl alochol, lignosulfonates and others. Acrylamide base commercial flocculents have been claimed effective in concentrations of approximately 0.2 lb per ton of solid (cost of the flocculent is about $1.00 per pound). In sludges with "moderately bonded" colloidal water adequate dewatering may be achieved by gravity thickening with the addition of inert weighting additives (e.g. soils, fly ash, etc.). The use of quicklime (CaO) instead of hydrated lime ($Ca(OH)_2$) may help in the destruction of the colloidal texture of the sludge.

Gentle vibration may ease the separation of solids from liquids and improve the performance of the thickening operation.

The sludge cakes from vacuum filtration or centrifuging will be broken into pieces to pass 1/4 in. mesh sieve but be retained by 200 mesh sieve. They may have or may not have enough coherence and rigidity for use as an aggregate in the formation of the "sludge-concrete". Sludge conglomerates too loose for cementation may need additional consolidation for achieving the necessary coherence and rigidity. This can be done by sludge rolling,

an operation simulating the powder rolling used in powder metallurgy. By this operation the particles are consolidated into a coherent mass of definite size and shape. In the sludge rolling, the sludge conveyed either horizontally or vertically through a set of steel rolls, may be compacted in the roll gap and will emerge as a sheet. In the rolling operation compaction occurs essentially only in one direction since very little pressure is transmitted sideways. The strength of the roll-compacted sludge will depend on its characteristics, kind and amount of the binder added in the dewatering operation and it will be the limiting factor for both the thickness and width of the sheet. Roll size, gap, speed, and rate of the sludge feed are the major factors to be controlled.

The roll-compacted sludge sheet can be broken into pieces (minus 1/4 in. mesh, plus 200 mesh) for use as an aggregate. Also, it may be cut into rectangular pieces. These pieces piled up to a certain height, one on another, may be subsequently covered on the outside with a layer of a soil-cement concrete, 0.5 to 2.0 in. thick (2 in. at the bottom and 0.5 in. on the sides). Brush or spray impregnation of the surface pores of the soil cement concrete with bitumen or paraffin will render the block resistant to leaching and ready for disposal.

An alternate procedure may involve bonding the rectangular pieces together with a lime-sand (ratio 1: 3) or lime-portland cement-sand (ratio 1:1:6) mortar.

Some improvement of coherence of sludge conglomerates obtained from filtration may be expected also by rinsing them alternately with lime emulsions and solution of magnesiums and zinc fluorosilicate.

Cements for Cementation of Sludges. The following criteria will govern the selection of the cements or cementitious mixtures for stabilization of toxic sludges:

(1) site of ultimate disposal (land or ocean dumping);

(2) cement performance, particularly its compatibility with the sludge aggregate chemicals;

(3) local availability;

(4) cost per weight or volume unit of the stabilized sludge.

The role of cements in the "sludge-concrete" is the same as in normal concretes (i.e. sand-rock-cement); namely, to create a cementitious matrix which embeds the compacted sludge conglomerates. The applicability of well established commercial cements, such as portland cement, lime and plaster of paris for bonding sludge conglomerates must be considered first.

Commercial Cements. The outstanding performance of portland cement in concrete construction is well known. Pricewise: (about 1¢/lb) it is one of the lowest cost products of the kind on the market. What is important for its application in the "sludge-concrete" is consideration of the extent to which the presence of different inorganic or organic compounds in the sludge conglomerate and mixing waters may be deleterious for setting and curing. Harmful substances that may be present in conglomerates include organic impurities, silt, clay, coal, lignite and certain lightweight and soft particles. Organic impurities may delay setting and hardening of concrete. Small percentages of certain organic impurities such as sugar may actually prevent the setting of portland cement for several days. Other organic impurities such as peat, humus, and organic loom may not be as serious but should be avoided. Materials finer than those passing the No.200 sieve, especially silt and clay, may be present as dust or may form a coating on the aggregate particles. Even thin coatings of silt or clay on gravel particles may be harmful because they may weaken the bond between the cement paste and the aggregate particles. The same may apply to certain inorganic salts either dispersed from poorly consolidated sludge conglomerates or present in the mixing water due to leaching. Salts of manganese, tin, zinc, copper and lead are active. Other salts that are potential retarders include sodium borate, sodium phosphate, sodium iodate, sodium sulfide and others.

In normal concretes, cement paste (cement plus water plus air) ordinarily constitutes 25 to 40 percent of the total volume of concrete (7 to 15 percent by volume of cement). Probably the same amount by volume may be needed for "sludge-concretes".

Plaster of paris is used as a cementing agent in gypsum concrete which consists of calcined gypsum, inorganic aggregate such as perlite (siliceous volcanic glass), vermiculite (micaceous mineral) or sand and wood chips or shavings. The applicability of plaster of paris or other calcined gypsum products without additives for cementing sludge conglomerates is an open question. Pure plaster of paris sets (initial hardening) in about 30 minutes but impurities and age of the plaster may introduce considerable variations. Set can be advanced by the use of accelerators such as small quantities of hardened plaster, zinc sulfate, potassium sulfate, common salt, alum or sodium carbonate. Retarders are borax, tartaric acid, citric acid, acetic acid and certain organic substances; ordinary glue dissolved in the mixing water is one of the most widely used retarders.

Among the precautions applicable to the use of plaster of paris is: avoidance of dry-outs, and freezing prior to hardening. The plaster must be permitted to hydrate before drying out, otherwise it will be strengthless and chalky. As soon as the plaster has had a few hours to harden, however, it should be dried out by ventilation or the circulation of warm air. Drying temperatures below 100 C will not harm the plaster.

By impregnating plaster of paris with resins (phenol- or urea-formaldehyde) either before or after casting, the strength may be increased. making the plaster suitable for cementing of sludge conglomerates. At the cost of $3.50 to 4.00/ton the plaster of paris is attractive. The price of urea-formaldehyde resin, if prepared on the spot from urea and formaldehyde, may be below 6¢/lb. Generally, 1 to 10 percent of resin is added to the plaster.[6] Addition of 5 percent resin would raise the cost of plaster to about $9/ton.

Lime is a general term covering the various chemical and physical forms of quicklime, hydrated lime and hydraulic lime. The lime products of building construction are mainly mixtures of hydrated lime with sand to form mortars, stuccos, plasters, sand-lime brick and silica-lime brick. Hydrated lime is often blended with gypsum plaster and is also used as a workability or plasticizing agent in concrete.

For bonding sludge conglomerates lime putty alone or a mixture of lime putty with portland cement may be useful. Lime putty is prepared from quick-lime (CaO) by slaking with more water than required for forming hydrate $[Ca(OH)_2]$ and aging. The approximate volumetric proportion of lime to sludge conglomerate may be similar to lime/sand in mortars; namely, 1:3. If portland cement is added the proportions may be:

Lime: portland cement: conglomerate = 1:1:6
or 2:1:9

The amount of water should be kept at the minimum required for workability; excess water weakens the product and increases drying shrinkage. Lime will not harden under water unless it contains impurities such as clay or silica. The rate of hardening of pure lime depends upon the rate of annexation of carbon dioxide from the atmosphere. Dolomitic limes also may be used for stabilization of soils.

The cost of lime depends upon the cost of limestone (calcium carbonate, about $1.00 to 1.50/ton) and the cost of calcination and slaking.

Coal tars and pitches, as well as asphalts, have been successfully used in concrete paving and stabilization of soils for many years.[4] For stabilization of soils the amount used varies from 4 to 10 percent depending upon the gradation and composition of the soils. Protection from the action of bacterias is important. Pricewise, they are attractive: the price of asphalt cement is about $20/ton.

Low Cost Cementing Materials for Stabilization of Sludges. A mixture of lime with siliceous materials such as silica, clay or soil reacts slowly with the formation of calcium silicates having bonded properties. The following procedure may be envisaged for stabilization of sludges; a non-airslaked quicklime is added to a partially dewatered sludge containing 10 to 30 percent water in a wooden mold, slaked with one part of the remaining water and allowed to age to form a lime putty (contaminated with the sludge solids) under cover of plastic for prevention of the access of CO_2 from air. Graded soil (in the range of particle size -4 and +200 mesh) or clay is added (the optimum ratio of lime to soil to be determined) and the entire content of the mold thoroughly blended. Compacting of the mold content may be achieved by vibration.

Setting and hardening may take several days. Some heating with steam, if applicable, would accelerate setting and hardening. The hardened block may be expected to require a coating for prevention of leaching of hazardous sludge components.

Undersintered cements of composition similar to portland cement but calcined at much lower temperatures exhibit hydraulic properties also; but with prolonged setting time and inferior strength properties. Such cements may be prepared by mixing limestone with clay or shale and burning at a temperature range of 850 to 950 C (portland cement requires firing of the order of 1600 C). The lower heat treatment will reduce the price of the cement.

Sulfoaluminate cements are of interest for bonding sludge conglomerates in regions abundant in low grade ferruginous bauxites (e.g. Oregon) or high alumina clays, or where waste tailings from alumina production are disposed of and may be available as a raw material. Calcium sulfoaluminate cement may be obtained by burning a batch composed approximately by weight of 1/2 gypsum, 1/4 aluminous mineral (tailings, bauxite, clay) and 1/4 chalk at about 800 C. The resulting product, a mixture of calcium aluminate sulfates exhibits hydraulic properties and hardens with water into the compound $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$ which should form a matrix for incorporating sludge solids.

Pozzolanic-type cements are of interest in regions such as California, where pozzolanic-type materials such as volcanic tocks, diatomaceous earth, etc., are abundant. ASTM C219 defines a pozzolanic as a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided forms and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties. A number of natural materials such as diatomaceous earth, opaline cherts and shales, tuffs and pumicites and some artificial materials such as fly ash are used as pozzolans. The use of pozzolans as cement replacements can substantially reduce the early strength of concrete, especially during the first 28 days. Because of the slow pozzolanic action, prolonged continuous wet curing and favorable curing temperatures must be provided.

Flyash is sometimes used as a pozzolanic admixture. Pozzolans may be mixed with portland cement to reduce its cost.

Low Cost Coatings. The "sludge-concrete", formed from sludge solids compacted into conglomerates and inorganic cements or cementitious bonding agents, may be expected to have fairly low surface erosion resistance and perhaps exhibit higher leachability of the hazardous sludge elements than desired. Optimization of the water/cement ratio, or optimization of conglomerate gradation cannot result in a water-tight, sludge-concrete unless the aggregate is water impermeable, and this may not be expected from sludge conglomerates. These deficiencies of the "sludge-concrete" must be remedied prior to its final disposal. A promising method for surface finishing of the "sludge-concrete" includes two stages:

(1) surface hardening with fluorosilicates;

(2) filling the pores or covering the surface with a water impermeable or water repellant coating.

Well established processes of hardening concrete surfaces with fluorosilicate solutions seems suitable for the sludge-concrete also. If portland

cement or an excess of calcium hydroxide was used as cements the surface may be directly coated with the fluorosilicate solution. Hydrolysis of the portland cement components, tri- and di-calcium silicates, will provide the necessary calcium hydroxide. Otherwise the surface of the sludge-concrete must be first impregnated with an emulsion of calcium hydroxide (approximately 2 lb of hydrated lime per gallon of water). The surface is then treated with a solution of magnesium and zinc fluorosilicate having the approximate composition:

Water	1 gallon
Zinc fluorosilicate	0.5 lb
Magnesium fluorosilicate	2.0 lb
Wetting agent	0.1 percent of the solution

The following reactions will occur:

$$ZnSiF_6 + 3Ca(OH)_2 \longrightarrow 2CaF_2 + ZnF_2 + CaSiO_3 + 3H_2O$$

$$MgSiF_6 + 3Ca(OH)_2 \longrightarrow CaF_2 + MgF_2 + CaSiO_3 + 3H_2O$$

Formation of insoluble fluorides and silicates impart to the surface outstanding hardness and abrasion resistance. The procedure is relatively inexpensive: 1 gallon of solution (estimated cost below 40¢) may suffice for three coatings of two (1 cubic meter) blocks of the sludge-concrete.

A simple and efficient filling of the remaining pores of the sludge-concrete after its surface hardening may be achieved with the application of high-melting paraffin. The surface of the concrete will be heated with hot air and molten paraffin brushed into the pores. The method has been claimed as efficient for preventing capillary penetration of water. If the concrete contains large cracks of openings, they must first be filled with a cement grout. The amount of paraffin per 1 cubic meter of the sludge-concrete will depend upon its porosity, and probably will vary from 1 to 4 lb. The current price of paraffin is about 6¢/lb.

Bituminous paints, portland cement paints, coal tar epoxy coatings present an alternate solution for preventing leaching of hazardous

elements from the sludge-concrete. Asphalt or coal tar coating may be applied either cold or hot.[7] Two coats are generally applied, a thin priming coat to ensure bond and a thicker finishing coat. The thickness of each coat is below 1 mm.

Black varnish consists of soft pitch fluxed back to brushing or spraying consistency mixed with coal tar naphtha. It has been used for protection of industrial steel work and as antifouling marine paint.

Portland cement paints are a composition of either pure portland cement or portland cement with hydrated lime (up to 25%) and water repellant agent such as calcium or aluminum stearate (about 1%). They reduce the water permeability of concretes and are commercially available.[8]

Coal tar or pitch/epoxy and coal tar/polyurethane coatings are superior in quality but higher in price.[8] These pitch/resin coatings consist of soft pitch, and epoxy or polyurethane resin, a suitable hardener, a mineral filter, and a volatile aromatic solvent. These components are mixed to give two parts: one containing the resin and the other the hardener (curing agent). Usually, 3 parts of tar and filler are used for 1 part of resin. A curing agent is used in an amount of 5 to 10 percent of the total weight. In spite of the relatively high price of the epoxy or urethane resins, the method may be still economical because of the low thickness of the required coatings (0.4 to 1.0 mm).

4. Recommended Program

The recommended program encompasses two phases. In the first phase investigations will be performed to establish the feasibility of several alternative operations involved in the cementation of heavy metal sludges or slurries with the use of inorganic or mineral cementing materials. These studies will be performed on a simulated sludge containing about 50 percent water and 45 percent solids, such as lead arsenate, cadmium sulfide and mercury sulfide, and about 5 percent colloidal clay. The sludge will be either

partially or totally dewatered*.

Inorganic cement e.g. portland cement or cementitious materials (e.g. lime and pozzolan) will be mixed with partially dewatered sludge and the mixture placed in a plastic or wooden molding for setting and hardening.

In a second approach, the totally dewatered sludge will be consolidated into conglomerate. After crushing and grading, the conglomerate will be blended with cement and water and allowed to set and harden in a plastic or wooden mold. The time of setting and hardening will be determined for different cementitious materials.

The set and hardened specimens will be subjected to the following testing:

(1) leaching resistance in ocean water

(2) leaching resistance in water saturated with CO_2, O_2 and containing 3 percent H_2S (simulation of aggressive ground waters)

(3) compression strength

(4) erosion resistance to water streams.

Specimens will be suspended in a flow of water of certain linear velocity. Their weight will be determined as a function of time.

The feasibility studies on inorganic cementation of heavy metal sludges will include:

(1) Investigation of practical application of partial or total dewatering of sludges by sedimentation, filtration and/or coagulation;

(2) feasibility studies of forming sludge conglomerate, by either physical or chemical methods, suitable for concentration. Filter cakes obtained from vacuum or pressure filtration with or without addition of binders and roll pressed compacts will be tested as aggregates. The possibility of increasing the hardness of soft filter cakes by treatment with fluorosilicate solution will be investigated;

*The term "total dewatering" means removal of the fluid water, but not necessarily the entire content of H_2O, particularly not the water which may add to cohesion or plasticity of the solid.

(3) investigation of the applicability of tars or asphalts for cementing;

(4) investigation of the applicability of portland cement for cementation;

(5) investigation of the applicability of plaster of paris/ urea formaldehyde mixture for cementation;

(6) investigation of the feasibility of slaking quickline with sludge waters;

(7) investigation of the applicability of pozzolanic cements;

(8) investigation of the feasibility of surface hardening of "sludge-concretes" with fluorosilicate solutions;

(9) investigation of the feasibility of impregnation of "sludge-concrete" pore with paraffin or black varnish;

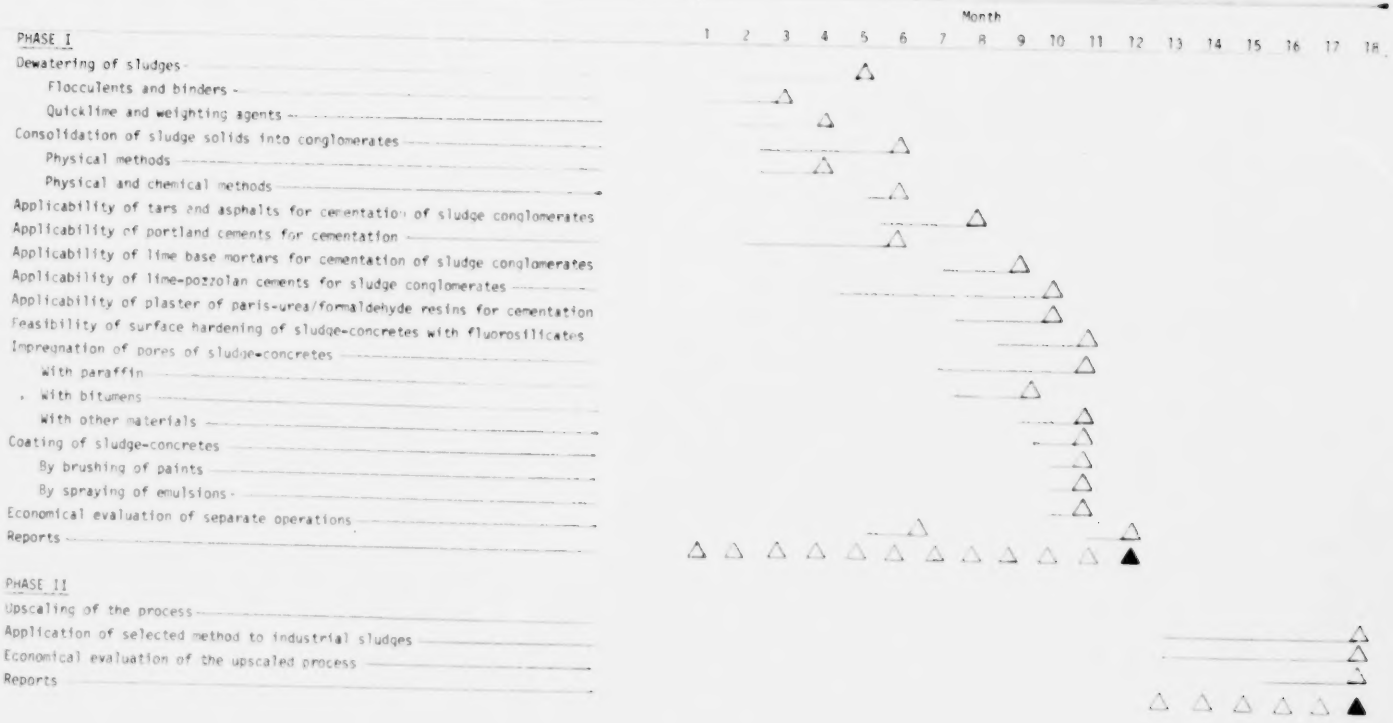
(10) investigation of the feasibility of coating and bituminous paints;

(11) technical and economic assessment of the above approaches and selection of the most promising for demonstration testing.

In Phase II of the program there will be a demonstration of upscaling of the most promising methods for cementation of sludges. A few hazardous industrial sludges in amounts of about 50 to 100 gallons each will be used for this purpose. A Detailed Economic and Technical Assessment of the best stabilization techniques will be performed.

It is estimated that Phase I of the program will take one year and Phase II six months. The complete two-phase 18 months program is estimated to cost about $150,000. Table 1 presents the proposed schedule.

TABLE 1.
PROPOSED SCHEDULE FOR TWO-PHASE PROGRAM


Month
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
PHASE I
Dewatering of sludges
Flocculents and binders
Quicklime and weighting agents
Consolidation of sludge solids into conglomerates
Physical methods
Physical and chemical methods
Applicability of tars and asphalts for cementation of sludge conglomerates
Applicability of portland cements for cementation
Applicability of lime base mortars for cementation of sludge conglomerates
Applicability of lime-pozzolan cements for sludge conglomerates
Applicability of plaster of paris-urea/formaldehyde resins for cementation
Feasibility of surface hardening of sludge-concretes with fluorosilicates
Impregnation of pores of sludge-concretes
With paraffin
With bitumens
With other materials
Coating of sludge-concretes
By brushing of paints
By spraying of emulsions
Economical evaluation of separate operations
Reports
PHASE II
Upscaling of the process
Application of selected method to industrial sludges
Economical evaluation of the upscaled process
Reports

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DEVELOPMENT OF LOW COST ORGANIC CEMENTATION APPROACHES FOR STABILIZING HEAVY METAL CONTAINING SOLID WASTES

In the preceding research plan inorganic cements are recommended for agglomerating and stabilizing heavy metal containing sludges prior to ultimate disposal in either a landfill or ocean burial environment. The inorganic cementation approach is attractive for waste materials containing significant water, since the wastes can be agglomerated and solidified without the need for separating the bulk of the water from the solids. On the other hand, the waste loading of these "sludge concretes" is expected to approach only 60 to 70 percent. There are many heavy metal containing wastes which are essentially dry (e.g., powders from bag houses, or residual arsenical pesticide wastes) for which it is felt can be more effectively stabilized at a much higher waste loading with organic cementation and coating procdures. This research plan addresses itself to the alternative approach of utilizing organic cements and coatings with an objective of obtaining stabilized agglomerates with a waste solids loading of greater than 90 percent.

Cementing and Coating Criteria

The primary technical considerations are:

(1) Initial resistance of the passified wastes to dispersion into the environment by the chemical and physical forces of nature.

(2) Long term resistance of the passified wastes to aging processes, these being bacteriological, chemical, and physical.

The stability of freshly passified wastes with respect to dispersion into the ecology will depend mainly upon the resistance of the wastes to diffusion through the agglomerate cement and coating, and the resistance of the coated agglomerates to counter diffusion of aqueous media. Such diffusion will be affected by the conditions of the final disposal environment.

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The passified heavy metal contaminants must resist dispersion into the environment not only initially but for a long period of time as well. Consequentially, bacteriological action is an important consideration when agglomerated wastes are placed in the earth for final disposal. Although underground, radiation resistance should also be estimated because of possible radiation degradation in preparation, transportation, and handling. The laboratory effort therefore must establish the effects of bacteriological, radiative, and chemical degradative forces as well as those of the leaching action of natural water.

Selection of Materials for Cementing and Coating

Materials selected for passivation of dry heavy metal containing wastes must satisfy the criteria previously given. In addition, they must be inherently low in cost. Cost is minimized, of course, when the selected organic cementation and coating materials are capable of yielding products having a high percentage loading content of metal contaminants.

Equal consideration must be given to ease of processing the passified products. It is desirable that simple equipment be employed, and that processing be uncomplicated so that a detailed procedure for passivation is not necessary.

In the light of the performance and cost criteria, materials for cementing and coating dry heavy metal wastes were selected mainly from among organic resins, particularly the olefinic resins. Polyolefins are hydrophobic and they resist bacteriological degradation. They can be made resistant to intense ultraviolet radiation, and they can be chemically cross-linked, a property that contributes to products meeting high chemical resistance standards. In addition, they are relatively low cost, stemming from the petrochemical industry; and commercial resins, in the main, are recognized to be nonhazardous. Furthermore, polyolefins readily wet solidus material due to their low surface tension and hydrophobic properties. Thus a small amount of resin can be suitable for effectively cementing a large quantity of metal contaminants and subsequent coating of the agglomerated formations.

The proof-of-principle experimentation utilized polybutadiene oligomers and powdered polyethylene for formation of heavy metal waste containing products. These resins were selected after careful consideration of commercial polyolefins in the light of the objectives of this work. Although polyolefins such as pitch, tar, and polyethylene have been employed for this purpose by other workers, the use of polybutadiene oligomers and powdered polyethylene, is believed to provide significant advantages in carrying out heavy metal passivation. The oligomers required here can be prepared at low cost from butadiene, and waste polyethylene.

Let us first consider polybutadiene oligomers. These resins have moderate molecular weights and are commercially available. Furthermore, they may be obtained with terminal, chemically functional groups, (hydroxyl and carboxyl groups). Being hydrocarbon in nature and of moderate molecular weight, the resins are capable of being blended with large amounts of solidus material. Utilizing the terminal functional groups, the molecular weignt of these materials may be increased markedly by chemical coreactants. Desirable high molecular resins are thus fashioned in the presence of the solidus filler. This advantage negates the task of blending filler into high molecular weight resin, a difficult task due to the high viscosity of such materials.

The resulting agglomerates obtained through the above procedure may be tailored to exhibit the desired stiffness. For this purpose, the pendant unsaturation of the resin can be utilized as well as its terminal groups. Employing peroxides and/or polyfunctional chemical coreactants, the stiffness of the agglomerated contaminants is tailored to satisfy the technique of coating and the requirements of long-term disposal.

Powdered polyethylene is employed in powder coating the agglomerated contaminants. The solventless technique of powder coating is presently gaining increased importance in material coating operations due to recent governmental legislation restricting the venting of solvents into the atmosphere. At the present time, many resins are being offered commercially

in response to this need in powder coating. In our opinion polyethylene best satisfies cost and performance criteria and therefore is potentially the material best suited for sealing agglomerates of heavy metal contaminants.

The purpose of the two-step operation consisting of cementing and coating as described above is the preparation of passified waste products containing waste loadings significantly greater than previously realized. The methods employed previously in the disposal of low level radioactive waste consisted of simply blending the contaminants into resins. Products containing more than 40 percent by weight of solid waste were difficult to obtain with previously attempted techniques due to the high viscosity of such systems. Furthermore, these products often exhibited uncoated contaminants on their surfaces which could be dispersed into the environment by water leaching. It was anticipated that the above described two-step operation (thermoset cement plus thermoplastic coat) could at least double the solids loading and would eliminate the problem of uncoated surfaces.

Proof of Principle Experimentation

In order to assure the formation of ultimate disposal products which resist leaching, it is prudent to tailor the heavy metal wastes to exhibit the least inherent solubility in water. In the framework of cost limitations, this operation is definitely desirable, and in practice this procedure will be invoked. For the purpose of testing cementing and coating materials, however, such testing is more meaningful when results are obtained with respect to very water soluble materials. Therefore, the resins for use in heavy metal passivation were evaluated using highly soluble sodium chloride as the "simulated" waste. Techniques were developed for preparing very integral stable products with a high solids loading (Figure 1). The products contain a core consisting of salts (NaCl) residing in a matrix of thermoset polybutadiene. The exterior coating material is polyethylene which results from the fusion of powdered polyethylene on to the core.

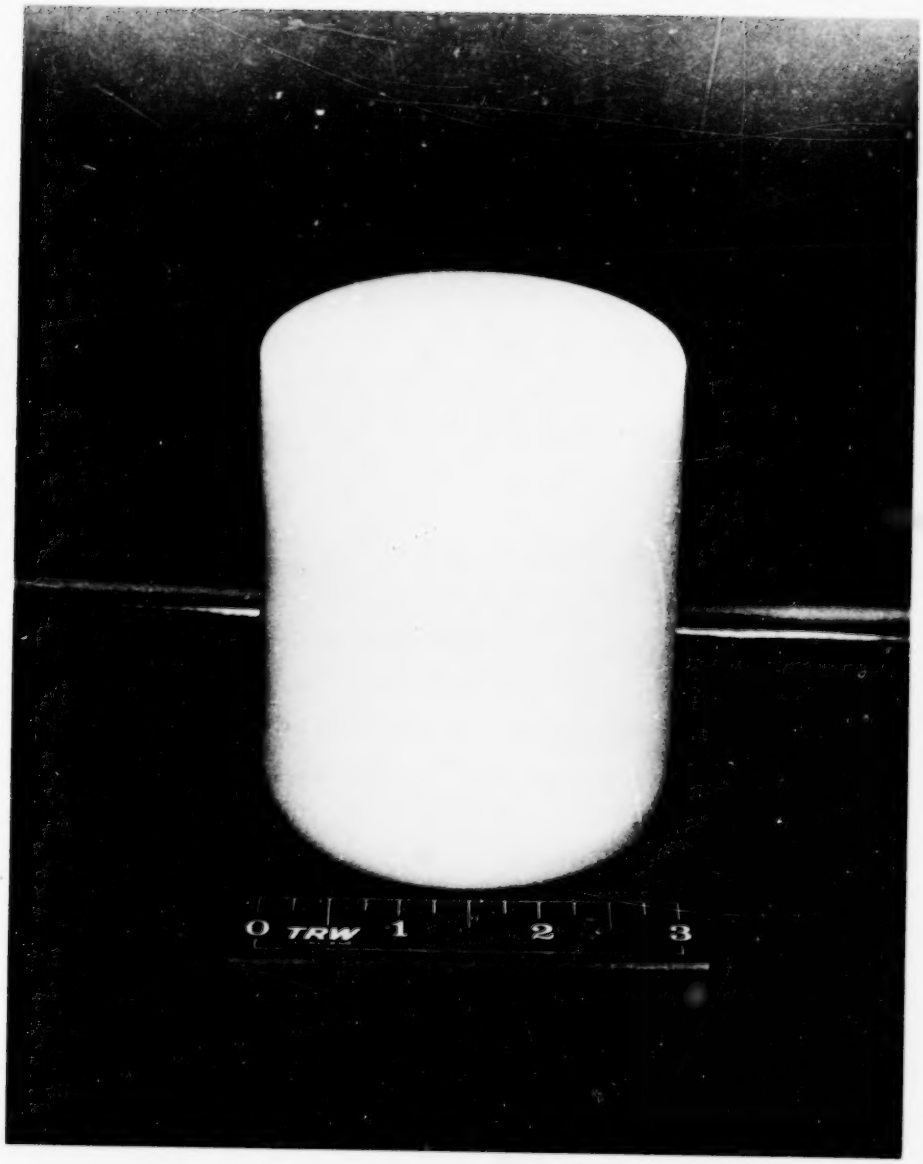

Figure 1. Sodium chloride filled test specimen.

The dimensions of the cylindrical products were 3-1/4 x 3-1/2 inches. This size was found to be convenient for handling and testing in the laboratory effort. In practice, larger blocks, about 36 x 36 x 36 in. square can be readily produced.

The above constitutes a description of the preferred products, as they resulted from a study of resins and techniques systematically screened in proof-of-principle experimentation. For reasons given previously polyolefinic resins were the preferred materials at the onset of the program. The resins yielding the most satisfactory products stemmed from polybutadiene oligomers with carboxyl terminal groups, whose microstructure contained unsaturation of which approximately 85 to 90 percent was of the pendant, vinyl configuration.

Epoxides were employed for the purpose of significantly increasing the molecular weight of the oligomers in the presence of the salt waste simulant. These epoxides represented about 10 percent by weight of the composition of the resinous matrix of the core and stem from diglycidyl ethers of phenol A. These materials represent the preponderance of the low cost commercial epoxides. Low cost peroxides were also employed to the extent of 1 percent of the composition for the purpose of stiffening the core composition in order to render it dimensionally stable for use in the subsequent operation of fusing powdered polyethylene onto the core.

With respect to deciphering the preferred techniques, the roles of the polyolefinic resins employed was interchanged with respect to their functioning as core and/or coating materials. Polybutadiene was found to be ineffective as a coating material because upon thermosetting the concomitant shrinkage occurring caused flows upon the surface. These flows lead to improperly sealed cores. When powdered polyethylene was fused with salt in order to form the core, it was found that this arrangement did not properly seal the salt, and when additional polyethylene was employed in order to form a coated core, the core arrangement was not dimensionally stable under the temperatures of fusion, consequently salt penetrated to the surface of the product.

One question stemming from the program of deciphering the preferred technique was whether polyethylene could be coated onto a core consisting of salt and a thermoplastic resin having a melting point greater than polyethylene. This approach was ruled out on three counts because: (1) the thermoplastic resins having greater heat resistance are not low cost, (2) the desirable high filler content products are not readily obtained due to the viscous nature of these thermoplastic materials, and (3) the core materials stemming from salt-powder resin fusion did not yield salt effectively coated by resin, especially so when fashioning high salt content arrangements. As a consequence of the latter phenomenon, the resins employed for coating the core must adhere to salt as well as resin in order to effectively seal the core. Due to the markedly dissimilar chemical nature of salt and resin, adherence did not occur, thereby a flow was formed which lead to the delamination of the coating. In contrast, the fluid polybutadiene oligomers yielded a resin coated salt even at high salt content. The salt is entrapped into the resinous matrix and consequently, provides a more effective base for sealing of the core.

Products were prepared using the preferred technique of thermosetting core and thermoplastic coating containing sodium carbonate and sodium chloride up to 87 percent by weight. The resistance to weight change of these products subjected to the leaching action of aqueous 0.1 HCl was observed over a period of thirteen days. The products were weighed after periodic removal from the solution, patted dry with paper towels, and allowed to air dry. The stability of the products as indicated by retention of weight was found to be excellent. No significant weight change was found with many of the samples after the leaching tests.

Recommended Research and Development. It is recommended that a Phase I Program consisting of four tasks be initiated:

Task I — Preparation of molds designed for fashioning agglomerate and fusing powdered resin into 6 x 6 x 6 in. cubes of material.

Task II — Preparation of 6 x 6 x 6 in. coated samples containing a water soluble salt content of 90 percent by weight.

Task III — Long term testing of the products in aqueous leaching media.

Task IV — Economic assessment

In Task I simple 6 x 6 x 6 in. rectilinear molds will be designed and fabricated. Emphasis will be placed on designing low-cost molds which are readily scaleable to larger sizes (e.g. 18 x 18 x 18 in.). It is believed that a rectilinear configuration is more desirable than a cylindrical configuration since rectilinear blocks represent a more effective utilization of space in the ultimate disposal environment.

The Task II effort will involve the development of optimized mixing, casting and coating techniques for stabilizing both soluble and insoluble waste constituents. Olefinic oligomers with appropriate additives will be utilized as cementing materials and both commercial and waste polyethylene will be evaluated as block coatings. The objective is to obtain sealed agglomerate blocks containing greater than 90 percent solids loading. Utilizing the optimized techniques a number of 6 x 6 x 6 in. blocks will be prepared for laboratory leaching studies (Task III).

The Task III laboratory leaching studies will consist of a systematic exposure of the test blocks to simulated landfill and ocean burial environments. Landfill experiments will be conducted in outdoor test bins where the air-soil-water environment is controlled and modeled to simulate a typical California Class I landfill. Ocean burial experiments will be conducted in tanks through which sea-water is circulated and typical marine life is maintained. The landfill and ocean simulated environments will be regularly sampled to determine the extent to which hazardous waste constituents are leached from the test blocks. Testing will continue for at least 12 months after which the test block specimens will be removed and completely analyzed (destructively) to determine their stability.

The fourth program task will consist of a detailed analysis of the costs associated with stabilizing and disposing of heavy metal containing wastes by the organic cementation process. Comparison will be made of the costs and effectiveness of the polymeric bonding approach with alternative methods of preparing material for ultimate disposal (e.g. inorganic cementation, sealed vaults, etc.) and a cost benefit analysis prepared.

It is estimated that this Phase I Program can be completed in 18 months at a cost of about $150,000. Test specimens would be prepared in the first four to six months and tested in simulated ultimate disposal environments over the next 12 to 14 months.

DECONTAMINATION OF SOILS AND SILTS BY GASEOUS EXTRACTION

1. Problem Background

The fate of chemicals in soils is a subject of current national interest due to their role in environmental pollution. Agricultural pesticides have been singled out for special consideration since large quantities are being dispersed on major agricultural soils. As a consequence, soils represent a vast reservoir, receiving pesticides applied either intentionally or accidentally.

A second serious source of soil contamination, limited to certain regions but nevertheless very dangerous, resulted from manufacture and demilitarization of poisonous chemicals by the U. S. Army units. The exact amount of contaminated soils is hard to estimate. In the Rocky Mountain Arsenal--Basin A only--there are 1.3 million tons of soil contaminated with arsenic oxides, arsenic chloride, mercury halides and other inorganic chemicals. Many of the pesticides, specifically those containing heavy metals such as arsenic or mercury, exhibit a tendency to convert into inorganic compounds and assumulate.

Residual hazardous heavy metal compounds present problems from an agricultural and environmental standpoint. Many plants exhibit the capacity to absorb and convert them into food and fiber products. Pesticide residues have damaged crops, found their way into air and water, and consequently, have affected marine life and animal life. In some cases, pesticides have accumulated in the lower organisms and are magnified in concentration through food chains. Among the hazardous components present in the soil as contaminants, arsenic, mercury, and their compounds pose a particularly serious problem.

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2. Hazards from Arsenic and Mercury Compounds in the Soil

Inorganic arsenicals such as arsenic trioxide As_2O_3, arsenic pentoxide As_2O_5, sodium hydrogen arsenate Na_2HAsO_4, sodium arsenite ($NaAsO_2$ or Na_3AsO_3), dipotassium hydrogen arsenate K_2HAsO_4, lead arsenate $Pb_3(AsO_4)_2$, lead hydrogen arsenate $PbHAsO_4$, and paris green, $3Cu(AsO_2)_2 \cdot Cu(C_2H_3O_2)_2$, as well as organic arsenicals such as disodium methane arsonate, DSMA, $CH_3AsO(ONa)_2$ and cacodylic acid $(CH_3)_2AsO(OH)$, have been used as insecticides, herbicides, and soil sterilants for many years. Whereas the average arsenic content of the soil is below 5 ppm, arsenic concentration several hundred times this amount has accumulated in certain soils. Disposal of arsenic containing chemicals by the U.S. Army has resulted in waste lagoons with soil contamination by arsenic about 40 to 50 ppm. Arsenic chemicals converted into arsenate or arsenite salts may exist either as water soluble or water insoluble compounds. The water soluble compounds are the most toxic to plants and mammals. The insoluble materials such as iron arsenate ($FeAsO_4$), aluminum arsenate ($AlAsO_4$) or calcium arsenate are less phytotoxic.

Plants vary in their tolerance for arsenic. The least tolerant plants include peaches and apricots among the fruits; barley, wheat, peas, and beans among the field crops; and alfalfa, clovers, vetch and Sudan grass among the forages.

Arsenic toxicity is evidenced by slow, stunted growth and late maturity of plants. Shot-hole and marginal scorch occur on the leaves of the more sensitive fruits, notably peach and apricot. Legumes tend to die in the seedling stage, following the appearance of small spots of dead tissue scattered over the leaves. Grain crops turn yellow and die back from the tips of the leaves. Arsenic-poisoned corn seems to suffer from too little moisture. Arsenites seem to be more troublesome than arsenates.

Mercury oxide HgO and chlorides (Hg_2Cl_2 and $HgCl_2$) and the organic mercurials including methyl, ethyl, phenyl mercury derivatives, for example PMA (phenyl mercury acetate $C_6H_5HgOCOCH_3$) are being used as seed disinfectants,

for weed control, and as pesticides and germicides. Mercuric chloride has been applied to seeds both in the dry state and in solution. Mercurous chloride is less toxic to living organisms than mercuric chloride. Mercuric oxide HgO is relatively insoluble in water; it has been used for disinfecting white and sweet potato seed. Ethyl mercuric chloride is used as a fungicide. It sublimes easily. Ethyl mercuric phosphate $C_2H_5HgPO_4$, is water soluble and is used as a component of seed disinfectants. Bactericidal and fungicidal compositions of mercurials may be either liquid or solid. Solid compositions are compounded by blending the active mercurial ingredient with finely divided solids such as attapulgite clays, diatomaceous earth, synthetic fine silica, or flours derived from walnut shell, redwood, soybean, cotton seed, etc.

Mercurials undergo translocation in plants and animals; that is, a mercurial sprayed on a plant leaf or placed on seed will find its way to roots, the stalk and even the grain. Seed treated with mercury compounds bears grain containing considerably more mercury than untreated seed. Mercury from soil can be converted by bacteria to highly toxic methylmercury compounds which find their way through the food chains to mammals.

Mercury being an element cannot be detoxified in the same sense as many of the toxic but non-persistent pesticides which decompose in air and sunlight. Mercury and its compounds may be displaced from soil into river beds and become more hazardous due to possible methylation processes. The application of mercurous and mercuric compounds to soils could also result in the release of mercury vapor. The soil factors which would increase the rate of conversion of mercury salts to metallic mercury include greater moisture, organic matter content, pH, and temperature. Because of the high toxicity of this element and its components, the maximum concentration for mercury in soils should not exceed the ppb level. The accumulation of mercury through disposal of mercurial chemicals by the U.S. Army in certain soils is of the order of 40 to 50 ppm or higher, i.e., it exceeds several throusand times the allowable limit.

3. Soil as the Carrier of Arsenic and Mercury Contaminants

Soil is one of the most complex materials. The natural body is composed of minerals, disintegrated and decomposed rocks, and minerals mixed with organic matter in all stages of decay. Air and water are usually considered soil components along with the microflora.

Two main groups of minerals are found in the soil. In the primary group are those minerals that have persisted in the soil more or less unchanged from the original rock. Feldspars usually dominate the primary silicate minerals. Quartz dominates the resistant oxide groups with such oxides as zircon ($ZrO_2 \cdot SiO_2$), ilmenite ($FeO \cdot TiO_2$), gibbsite $Al_2O_3 \cdot XH_2O$ and hematite $Fe_2O_3 \cdot XH_2O$ being present in greater or lesser amounts. These minerals most often are found with particle size diameter of more than 2 microns and they make up the silt, sand and gravel of the soils. The minerals of the second groups have been changed by weathering and are referred to as secondary minerals. The most important of this group are the clay minerals which are present in various amounts. The secondary minerals are usually less than 2 microns in diameter.

The organic matter represents an accumulation of partially decayed and partially resynthesized plant and animal residues. The content is usually small--only about 3 to 5 percent by weight in the case of a representative mineral topsoil. It may reveal any stage of decomposition. It is generally divided into two groups: (1) the original organic tissue and its products of partial decomposition and (2) the more lignified protein complex, the humus. Usually, humus is brown or black in color, and colloidal in nature. Humus has a capacity to attract and hold water, gases, and ions. The adsorptive capacity of humus greatly exceeds that of any clay even that of montmorillonite. Humus is not a specific compound. Its adsorption capacity is attributed to the presence of carboxylic (-COOH) and phenolic (-OH) groups attached to a central unit of a humus colloid

(composed mostly of C and H atoms). Thereby the phenolic hydroxyl groups are connected to aromatic rings while the carbonylic groups are bonded to other carbon atoms in the central unit. The charge on humus colloids is pH-dependent.

Chemicals in the soils are subject to many complicated processes which generally may be divided into three classes:

(1) Physical Processes: Vaporization; leaching or movement by capillary water into the soil profile; photodecomposition; physical adsorption into various soil colloids.

(2) Biological Processes: Metabolism by soil microorganisms and root uptake, absorption by plant.

(3) Chemical Processes: Processes not mediated by the microflora of the soil.

At the soil surface, volatilization and photo-decomposition are important. Biological and chemical processes gain in importance after the chemicals move beneath the soil surface.

Among many processes and reactions occurring in and/or with the participation of the soil component, adsorption is one of the most important in the governing of the behavior of the metallic components within the soil. Physical adsorption means concentration at the soil surface or inside the capillary texture of organic and inorganic matter. Chemical absorption (by plants) means exclusion from the soil surface. Adsorption directly or indirectly influences the movement of hazardous contaminants, plant uptake, microbiological and chemical decomposition and volatilization. Components strongly adsorbed by soil components are not readily moved by water passing into and within the soil. When present at the soil surface, they are more susceptible to photodegradation and volatilization.

Soil organic matter usually is the component most highly correlated with adsorption, and retention against leaching. The second major soil components affecting adsorption are the crystalline layer silicate clays such as montmorillonite and vermiculite because of their high cation exchange capacities (80-150 meq/100 gram of soil) and high surface areas (600-800 M^2/g). Other clay minerals such as illite, kaolinite, halloysite, etc., and oxides and hydroxides of iron and aluminum may contribute to adsorption also. Fe- and Al- oxides and hydroxides develop a pH-dependent positive charge and may have high surface areas. Soils rich in Fe and Al content have high anion adsorption capacities.

In many soils, significant quantities of noncrystalline colloidal matter are found. Part of the iron and aluminum hydrous oxides, as well as part of silica, in some soils is amorphous. The most important amorphous matter in soils in allophane, a poorly defined combination of silica and alumina. Its composition approximates the formula $Al_2O_3 \cdot 2SiO_2 \cdot H_2O$. Allophane exhibits highly pH dependent ion exchange, capacity, both cationic and anionic.

The cationic exchange capacity of different soil components may be roughly illustrated by the following numbers:

Humus	200 milliequivalent/100 gram of soil
Vermiculite	150 milliequivalent/100 gram of soil
Montmorillonite	100 milliequivalent/100 gram of soil
Hydrous mica	30 milliequivalent/100 gram of soil
Kaolinite	8 milliequivalent/100 gram of soil
Hydrous oxides	4 milliequivalent/100 gram of soil

The power of the soil particles to bind both cations and anions makes it an amphoteric adsorbent. In general, the soils' particles carry a net negative charge which can be directly demonstrated by electrophoresis. This charge arises in two ways: By isomorphous ion substitution and by ionization of hydroxyl groups attached to silicon of broken tetrahedron planes: $Si\text{-}OH + H_2O \cdot SiO^- + H_3O^+$. Negative charges also originate from humus (-COOH, -OH) and phosphoric and silicic acids which constitute more or

less an integral part of the clay particle surface. The adsorption of arsenic and mercury compounds by soil components complicates their removal. The amphoteric character of soil as adsorbent enables adsorption of arsenic as cation (As^{++} for example in $AsCl_3$) or anion (arsenate AsO_4^{3-} or arsenite AsO_3^{3-}).

Lateritic soils (soils rich in Al and Fe) and H- and Ca- soils (resulting from cation exchange of H^+ or Ca^{++} cations, respectively,) exhibit enhanced capacity for adsorbing arsenate ions. The presence of iron oxide Fe_2O_3 and high pH (alkaline reaction) seem to favor conversion of arsenite ions into arsenate ions. Adsorbed arsenate ions can be partially replaced by phosphate or citrate ions. High arsenate adsorption generally involves a decrease in arsenite adsorption. The adsorbed arsenate ions are strongly fixed to the soil.

The chemical behavior of arsenic in soils resembles that of phosphorus. Both elements may be fixed in the surface soils if sufficient iron, aluminum or calcium compounds are available for reaction. They may act as antagonists toward each other. A high level of phosphate in nutrient solutions containing arsenic causes less arsenic to accumulate in plants because of antagonistic action. However, in soils, increasing the level of phosphate enhances arsenic uptake, because phosphate replaces arsenate from aluminum arsenate, becoming itself insoluble and making the arsenate soluble.

No direct information could be found about the sorption of the mercury component by the soil adsorbents. Both ionic and molecular adsorption may occur with the participation of both humus and mineral adsorbents. Sorption of mercury as Hg_2^{++} or Hg^{++} in exchange for common exchangeable cations usually present in soils such as Ca^{++}, Mg^{++}, H^+, K^+, Na^+ and NH_4^+ may be expected. The extent of this adsorption can be expected to depend on the soil texture, its composition, pH, etc. Several indirect indications on the adsorption of mercury compounds by an adsorbent functionally similar to that found in the soil support this view. Diatomite filters (opal-like siliceous residue $SiO_2 \cdot nH_2O$ of one-celled organisms) have been claimed to reduce mercury content in certain industrial wastes from 5 ppm to 0.5 ppm.

Some activated carbons were found efficient for the removal of mercury components. Synthetic carboxylic acid cation exchange resins are known to effectively adsorb mercury cations.

Mercury compounds located in the soil become even more dangerous if they reach the water table. Formation of highly toxic and soluble organic derivatives (such as MeHg or Me_2Hg) due to the action of microorganisms is highly probable. The toxicity of the latter compounds far exceeds the toxicity of elemental mercury and the inorganic mercury compounds.

4. Removal of Arsenic and Mercury by Gaseous Extraction

The removal of arsenic, mercury and their compounds from the soils presents a real technological challenge to a process engineer. The difficulties are manifold. The most essential are:

(1) Complex character of the soil as substrate for the contaminants and chemical, physico-chemical and biological interaction of the contaminants with the soil.

(2) Reduction of trace concentration of the contaminants in a multicomponent and reactive material (soil) requires application of highly selective reagents and processes.

(3) Huge tonnage of the treated soil and its relatively low market value (about $1/ton plus transportation cost, if any) limits the process engineer to application of the least expensive reagents, simplest operations and simplest equipment. Otherwise, the cost of decontamination may be excessive.

(4) Retain fertility.

The gas extraction process for the decontamination of soils from mercury and arsenic promises to overcome the above difficulties.

Description of the Process. The essence of the process is conversion of arsenic and mercury and all their compounds into volatile chlorides (arsenic trichloride, $AsCl_3$, and $HgCl_2$) by fluidized bed reaction between dry soil and a gas mixture composed of hydrogen chloride, hydrogen and small amounts of chlorine. This gas mixture may or may not be diluted by a neutral gas carrier such as nitrogen or nitrogen enriched air. Thermodynamic calculations (see next paragraph) show that the presence of chlorine is not necessary for converting either mercury or arsenic into respective chlorides. Its addition to the reactant gas mixture is dictated by the desire of facilitating the process, especially improving the kinetics of the reactions, and also converting the titanium values of the soil into volatile titanium tetrachloride.* Methyl alcohol or methyl chloride vapor in the amount of about 1 percent to 2 percent may be added to the reactant gas mixture also as reaction catalyst. Treatment of the soil with proper composition of the reactant gas mixtures will not affect any of the mineral components of the soil except titanium (which is desirable), and iron oxides. Formation of the hardly volatile ferric or ferrous chlorides (in the operation temperatures) would be disadvantageous to the process because of consumption of chlorine values and accumulation of chlorine in the soil. Fortunately, however, iron chlorides may be readily converted back to iron oxides and phosgene; the latter compound being a saleable by-product of the process. The organic matter of the soil is not expected to react chemically with the reactant gas mixture to any considerable extent unless, for some unusual reasons, it contains a lot of compounds with double bonds. Polysaccharides (cellulose, hemicellulose, starch, pectic substances) and lignins exhibit a sufficient degree of chemical resistance to most chemicals. On the other hand, physical adsorption of the gas mixture reactants on the soil will occur, particularly at low temperatures, but desorption will follow at a later stage of processing with the expulsion of volatile chlorides from the soil by heat at vacuum.

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*Titanium usually is present in the soils in the amount from 0.2 to 1.0 percent. It seems to be neither useful nor detrimental to the fertility of the soils.

Soil pulverized to minus 200 mesh screened and dried* (Figure 1 and Figure 2) is brought into contact in a fluidized bed reactor with a gas mixture of the following approximate composition:

Nitrogen	40 to 70 percent
Hydrogen chloride	20 to 50 percent
Hydrogen	4 to 12 percent
Chlorine	0 to 8 percent
Methyl alcohol	0 to 2 percent

Safety reasons require that the total nitrogen and hydrogen chloride be not less than 70 percent. One or two fluidized bed reactors may be needed. Thermodynamic calculations show that the desired reactions are feasible at room temperature, but no satisfactory rate of reactions is expected below 100 C. If the soil/gas reaction is carried out at moderate temperatures and pressures above 1 atm the reaction products $HgCl_2$, $FeCl_2$ and $FeCl_3$ will remain in the soil, and the very volatile $AsCl_3$ and $TiCl_4$ (as well as water vapor from chemical reaction) will be entrapped by the gas mixture. The volatile components may be separated from the gas mixture by cooling to ambient temperature. The gas mixture, after adjusting its composition and drying, is recirculated to the fluidized bed reactor. The comparatively less volatile reaction product $HgCl_2$ may be expelled from the soil by heating under vacuum at about 250 to 300 C. It may be recovered together with traces of $FeCl_3$ in a cold trap. Most of the iron chlorides will, however, remain in the soil. Heating of the soil under vacuum also will result in partial decomposition and carbonization of the organic matter. After expulsion of mercuric chloride, hot air is admitted to the soil (Figure 2). In this condition, the following reactions will occur.†

$$FeCl_2 + \underset{\downarrow}{C} + O_2 \longrightarrow FeO + COCl_2$$

(The carbon, C, comes from carbonization of organic matter)

$$2FeCl_3 + 3\overset{\uparrow}{C} + 3O_2 \longrightarrow Fe_2O_3 + 3COCl_2$$

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*The optimal sequence of operations as well as the optimum particle size and optimum reaction temperatures must be found experimentally.

†For thermodynamics of these reactions, see next chapter.

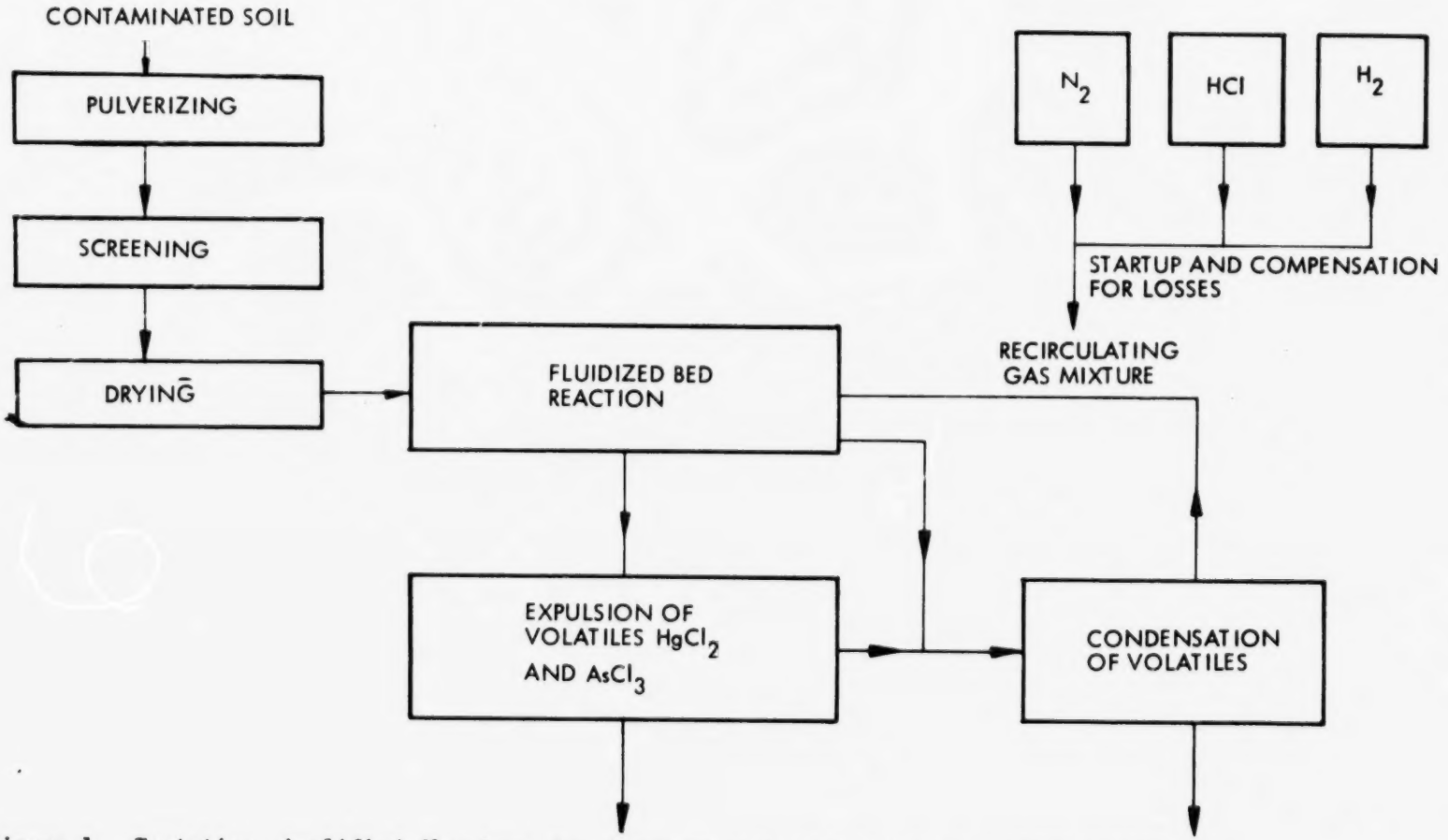


Figure 1. Tentative simplified flowsheet for decontamination of soils by gaseous extraction.

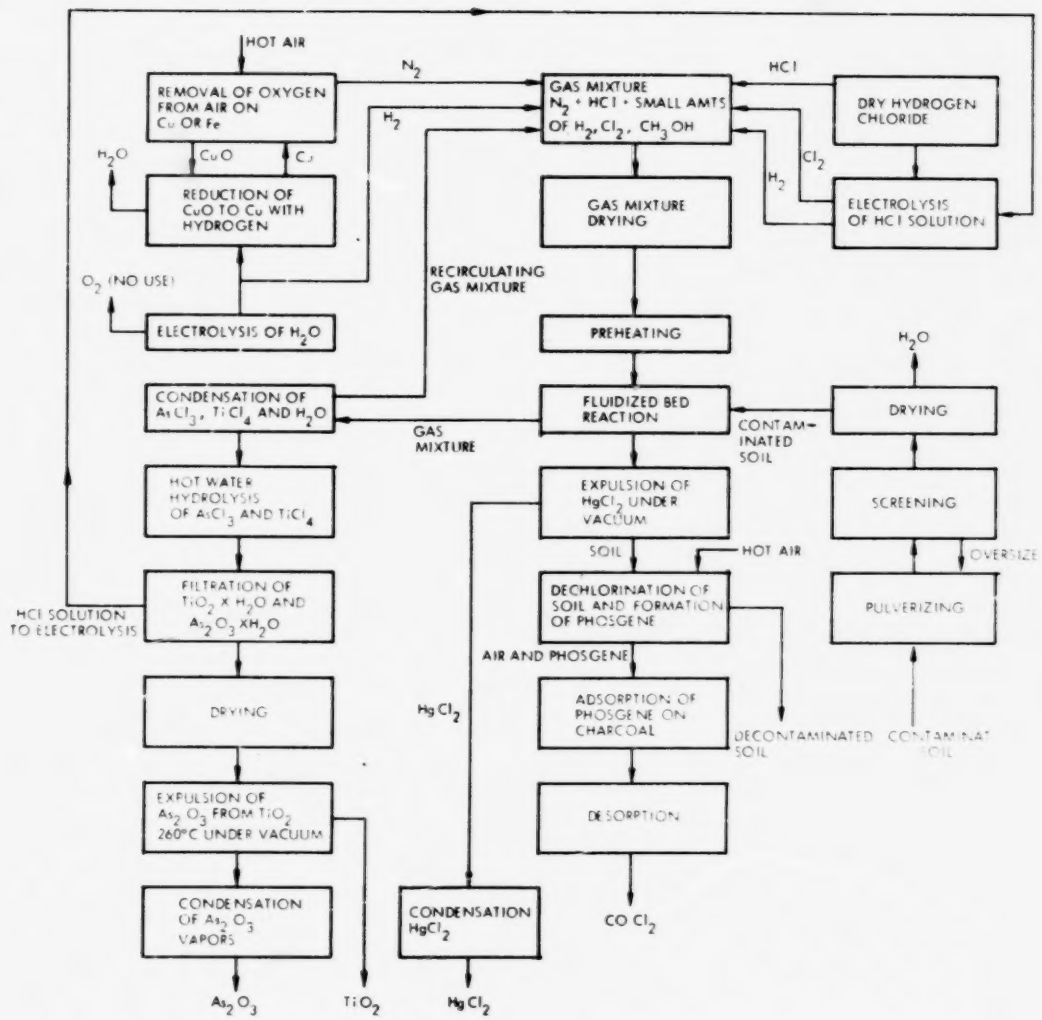


Figure 2. Flow diagram. Decontamination of soil by gaseous extraction of arsenic, mercury and excess chlorine.

The iron oxides will remain in the soil and phosgene will be entrained by air from which it can be quantitatively removed by adsorption with charcoal.

Condensed arsenic and titanium chlorides may be hydrolyzed by hot water at ratios not less than 20 moles of H_2O per mole $AsCl_3$. The following reactions will occur:

$$AsCl_3 + 3H_2O \rightleftharpoons As(OH)_3 + 3HCl$$

$$TiCl_4 + 2H_2O \rightleftharpoons TiO_2 + 4HCl$$

Boiling the solution and stripping it of HCl will shift the reactions to the right. After filtration the filtrate containing HCl solution is sent to electrolysis and the solid residue is dried and calcined at normal or reduced pressure for expelling As_2O_3, which is volatile, from TiO_2, which is not. At normal pressure, heating up to 450 C may be required. At 10mm Hg pressure, it is necessary to heat only to about 260 C. The gas extraction method of soil decontamination promises a number of advantages:

(1) the method is simple, fast and efficient;

(2) it requires little basic equipment (fluidized bed column and condenser);

(3) the process may be continuous;

(4) the decontamination units may be mobile for on-site operations;

(5) only moderate temperatures applied;

(6) recycling of the gas mixture limits the actual use of reactive gases to negligible amounts;

(7) no filtration or settling needed;

(8) the process is inexpensive; and

(9) in favorable conditions, the process presents the commercial option of extracting titanium values from the soil and producing the by-product phosgene. (Figure 2).

A mobile unit for decontamination of the soil by gaseous extraction in a fluidized bed may be mounted on a truck (Figure 3).

Physico-Chemical Aspects of the Process

The process takes advantage of the high volatility of several compounds and the considerable reactivity of arsenic and mercury compounds with hydrogen chloride and chlorine.

The volatilities of arsenic trichloride, titanium tetrachloride, mercury and mercury chloride are high (Table 1).

The calculated free energies of several reactions between the soil contaminants and the HCl-H_2-Cl_2-gas mixture are negative (Table 2).

The negative free energies of reactions (Table 2) imply that no free chlorine is needed in the reacting gas mixture for converting As and Hg compounds into their chlorides.

The calculated free energies of reaction of all mineral soil components with HCl-H_2 gas mixture, except iron oxides, are positive. Addition of chlorine to the gas mixture changes the sign of the free energies at certain concentrations (Table 3).

Except for iron oxide, no soil component, i.e., clay minerals, silica, alumina, etc., will be converted into chloride unless free chlorine is present in the gas mixture. Titanium compounds (ilmenite or dioxide) require lower concentration of free chlorine in the gas mixture $HCl + H_2 + Cl_2$ for forming titanium tetrachloride, than other soil components for forming respective chlorides (Table 3). Because of its high volatility in practice much lower concentrations of chlorine may suffice to get $TiCl_4$ in the gas phase. Ferrous and/or ferric chlorides may be expected among the reaction products. Reconversion of these chlorides back into their oxides may be expected to proceed easily with the formation of phosgene, provided enough reducing carbonaceous matter is present in the purified soil (Table 4).

Figure 3. Pictorial representation of truck mounted system

TABLE 1

VAPOR PRESSURE OF SEVERAL COMPOUNDS OF INTEREST
FOR THE SOIL DECONTAMINATION PROCESS

Compound	M.P. C	Temperature in C at which the indicated pressure is reached					
		1 mm	10mm	40mm	100mm	400mm	760mm Hg
As	814	372	437	483	518	579	610
$AsCl_3$	-18	-11.4	23.5	50.0	70.9	109.7	130.4
As_2O_3	312.8	212.5	259.7	299.2	332.5	412.2	457.2
$AlCl_3$	192.4	100.0	123.8	139.9	152.0	171.6	180.2
$FeCl_2$			700	779	842	961	1026
$FeCl_3$	304	194.0	235.5	256.8	272.5	298.0	319.0
Hg	-38.9	126.2	184.0	228.8	261.7	323.0	357.0
$HgCl_2$	277	136.2	180.2	212.5	237.0	275.5	304.0
$TiCl_4$	-30	-13.9	21.3	48.4	71.0	112.7	136.0
H_2O	0	-17 (ice)	11.3	34.1	51.6	82.9	100

TABLE 2
CALCULATED CHANGES OF FREE ENERGY OF REACTIONS BETWEEN
SOIL CONTAMINANTS AND HCl + Cl_2 + H_2 GAS MIXTURE

#	Reaction	ΔF at RT kcal	Remarks
1a	$As_2O_3 + 3H_2 + 3Cl_2 = 2AsCl_3 + 3H_2O(g)$	-163.1	
1b	$As_2O_3 + 6HCl = 2AsCl_3 + 3H_2O(g)$	-26.3	
1c	$As_2O_3 + 3H_2 = 2As + 3H_2O(g)$	-26.1	
1d	$2As + 3Cl_2 = 2AsCl_3$	-137.0	
1e	$As_2O_5 + 5H_2 + 3Cl_2 = 2AsCl_3 + 5H_2O(g)$	-225.4	
1f	$As_2O_5 + 2H_2 + 6HCl = 2AsCl_3 + 5H_2O(g)$	-88.6	
2a	$PbHAsO_4 + 7/2H_2 + 5/2Cl_2 = PbCl_2 + AsCl_3 + 4H_2O(g)$		No data available
2b	$PbHAsO_4 + H_2 + 5HCl = PbCl_2 + AsCl_3 + 4H_2O(g)$		
3a	$CaHAsO_4 \cdot H_2O + 7/2H_2 + 5/2Cl_2 = CaCl_2 + AsCl_3 + 4H_2O(g)$	-158	
3b	$CaHAsO_4 \cdot H_2O + H_2 + 5HCl = CaCl_2 + AsCl_3 + 4H_2O(g)$	-44	
4a	$Ca_3(AsO_4)_2 + 8H_2 + 6Cl_2 = 3CaCl_2 + 2AsCl_3 + 8H_2O(g)$	-391*	
4b	$Ca_3(AsO_4)_2 + 2H_2 + 12HCl = 3CaCl_2 + 2AsCl_3 + 8H_2O(g)$	-117*	
5a	$Ba_3(AsO_4)_2 + 8H_2 + 6Cl_2 = 3BaCl_2 + 2AsCl_3 + 8H_2O(g)$	-415*	Calculation was made for comparison
5b	$Ba_3(AsO_4)_2 + 2H_2 + 12HCl = 3BaCl_2 + 2AsCl_3 + 8H_2O(g)$	-141*	
6a	$Hg + Cl_2 = HgCl_2$	-42.2	
6b	$HgCl_2 + H_2 = Hg + 2HCl$	-3.4	
6c	$HgO + H_2 = Hg + H_2O$	-40.6	
6d	$HgSO_4 + H_2 = H_2SO_4 + Hg$	-23*	
6e	$HgSO_4 + 2HCl = HgCl_2 + H_2SO_4$	-20*	
6f	$HgSO_4 + H_2 + Cl_2 = HgCl_2 + H_2SO_4$	-65*	

* The free energy of formation of Ca or Ba arsenates have been assumed to be equal to 0.9 of the enthalpy ($\Delta F = 0.9\ \Delta H$)

TABLE 3
CALCULATED CHANGES OF FREE ENERGY OF REACTIONS BETWEEN THE SOIL COMPONENTS AND HCl + H_2 + Cl_2 GAS MIXTURE

#	Reaction	ΔF at RT kcal	% concentration of Cl_2 in HCl + Cl_2 + H_2 mixture for ΔF≤0
7a	$SiO_2 + 2Cl_2 + 2H_2 = SiCl_4 + 2H_2O(g)$	-53.3	
7b	$SiO_2 + 4HCl = SiCl_4 + 2H_2O(g)$	+37.9	17.0
8a	$Al_2O_3 + 3Cl_2 + 3H_2 = 2AlCl_3 + 3H_2O(g)$	-91.5	
8b	$Al_2O_3 + 6HCl = 2AlCl_3 + 3H_2O$	+45.3	16.5
	Clay minerals (kaolinite or halloysite):		
9a	$(2SiO_2)\cdot Al_2O_3\cdot 2H_2O + 7H_2 + 7Cl_2 = 2SiCl_4 + 2AlCl_3 + 9H_2O$	-185.	
9b	$(2SiO_2)\cdot Al_2O_3\cdot 2H_2O + 14HCl = 2SiCl_4 + 2AlCl_3 + 9H_2O$	+134.	21.4
10a	$Fe_2O_3 + 3Cl_2 + 3H_2 = 2FeCl_3 + 3H_2O(g)$	-145.7	
10b	$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O(g)$	-8.9	0
10c	$Fe_2O_3 + 3H_2 + 2Cl_2 = 2FeCl_2 + 3H_2O(g)$	-131.1	
10d	$Fe_2O_3 + 4HCl + H_2 = 2FeCl_2 + 3H_2O(g)$	-39.9	0
11a	$TiO_2 + 2Cl_2 + 2H_2 = TiCl_{4(l)} + 2H_2O(g)$	-66.6	
11b	$TiO_2 + 4HCl = TiCl_{4(l)} + 2H_2O(g)$	+24.6	12.7
	Mineral ilmenite:		
12a	$FeTiO_3 + 7/2Cl_2 + 3H_2 = FeCl_3 + TiCl_{4(l)} + 3H_2O$	-127.5	
12b	$FeTiO_3 + 6HCl + 1/2Cl_2 = FeCl_3 + TiCl_4 + 3H_2O$	+9.3	11.5
12c	$FeTiO_3 + 3Cl_2 + 3H_2 = FeCl_2 + TiCl_4 + 3H_2O$	-120.2	
12d	$FeTiO_3 + 6HCl = Fe\,Cl_2 + TiCl_4 + 3H_2O$	+16.6	6.3

TABLE 4
CALCULATED CHANGES OF FREE ENERGY - FORMATION
OF PHOSGENE FROM IRON CHLORIDES

No.	Reaction	Free energy change in kcal at temp. RT	400 K	500 K
13a	$2FeCl_3 + 3C + 3O_2 = Fe_2O_3 + 3COCl_2$	-169.4	-177.7	-171.8
13b	$FeCl_2 + C + O_2 = FeO + COCl_2$	-36.4	-36.8	-37.1

Laboratory Feasibility Study

In an experimental setup for the laboratory feasibility study of the soil purification process by gaseous extraction of the contaminants, the gas mixture from a gas manifold passed through a drying tower filled with drierite, into the fluidized bed reactor, and then into the condenser (Figure 4). The fluidized bed reactor was heated by wrapping the glass column with a heating tape. Temperature was controlled by a C/A thermocouple connected to a power controlling thermostating unit. The experimental fluidized bed reactor processed 30 grams of soil (Figure 5). The laboratory setup was calibrated at ambient and elevated temperature for the necessary gas flow for a given gas distributor and volume expansion of the soil sample. Studies were performed on agricultural soils contaminated with arsenic and Rocky Mountain Arsenal soil contaminated with arsenic and mercury. The reactive gases HCl, H_2 and Cl_2 were diluted with nitrogen. The concentration of the gas mixture and temperature were among the variables of the process subject to experimentation.

Stainless steel mesh, filter glass paper and glass frits, coarse, medium and fine, have been tried as gas distributors and specimen support in the fluidized bed column. Fritted glass, size fine (pore size 4 to 6 microns) performed satisfactorily and was used in all feasibility experiments.

In the calibration of the experimental unit the pressure drop across the gas distributor, or across the gas distributor and the layer of the specimen on it was correlated with the different gas flows at ambient temperature and at 150 C (Table 5). The expansion of the soil layer due to the gas flow was recorded at room temperature. The soil was not visible during operation at elevated temperature because the glass tube was wrapped with the heating tape. In most experiments, the decontamination of the soil was performed in two stages. In the first stage, the soil was contacted with the gas mixture. In the second stage, soil was heated under vacuum for thorough expulsion of the volatile contaminants.

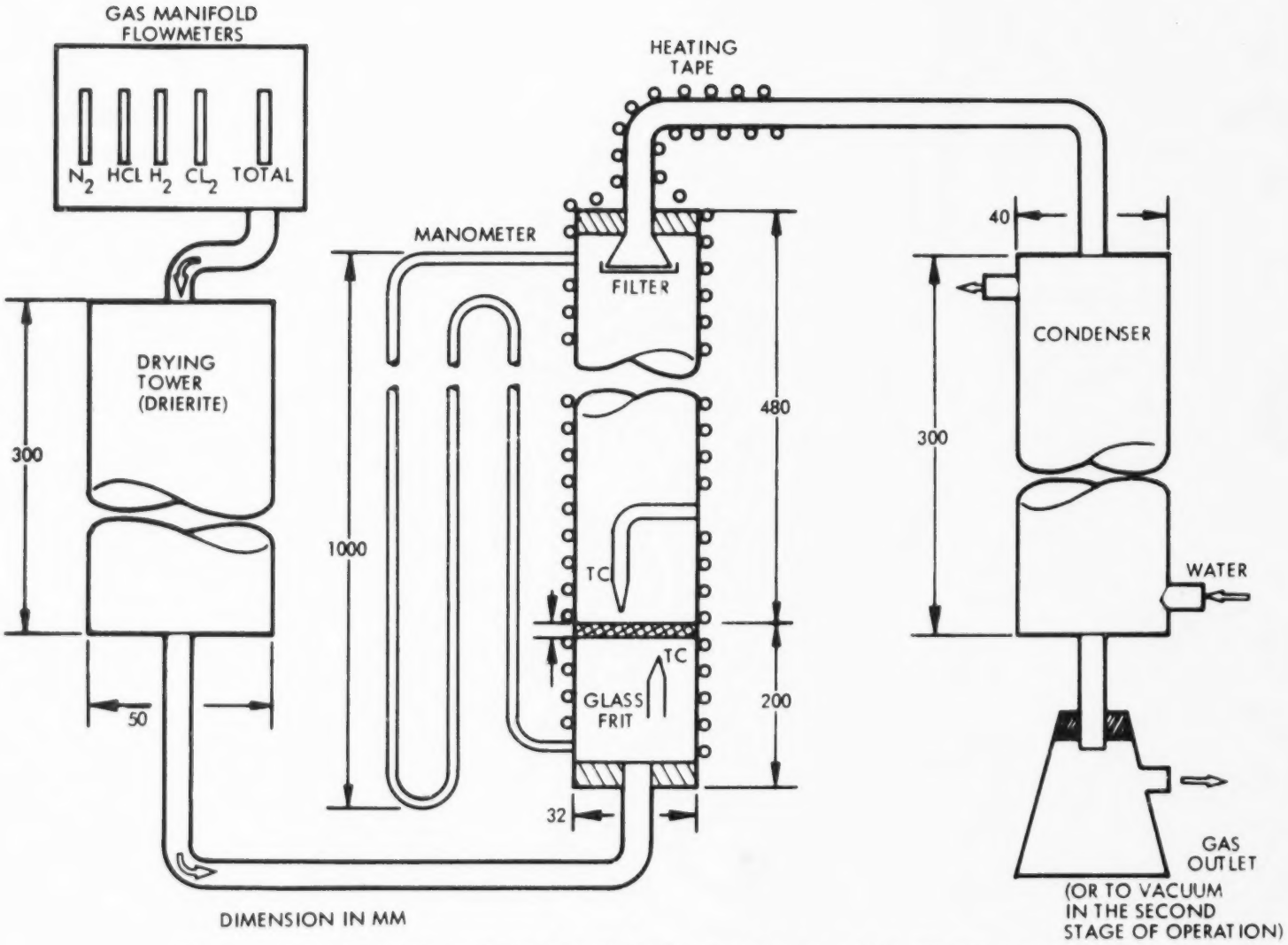


Figure 4. Laboratory set-up for decontamination of soils by gas extraction

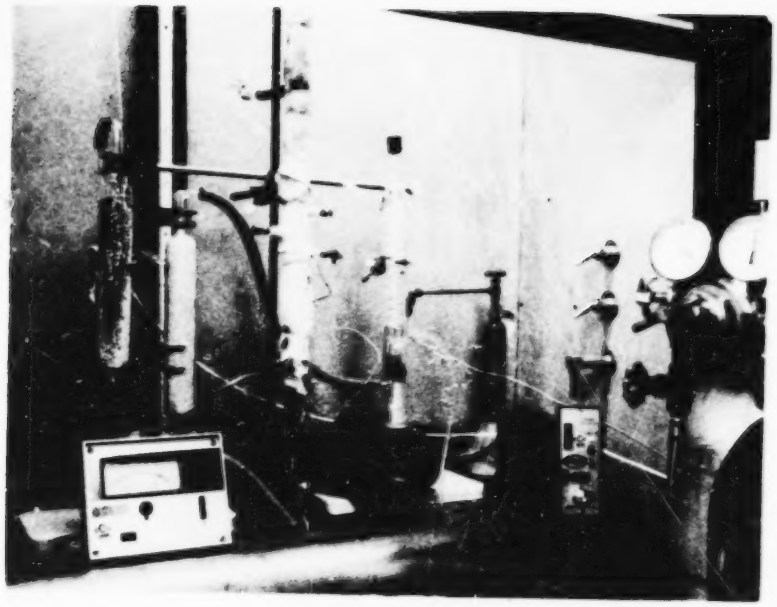


Figure 5. Laboratory fluidized bed reactor system.

TABLE 5

CALIBRATION OF THE LABORATORY SETUP FOR DECONTAMINATION OF SOILS BY GASEOUS EXTRACTION

Pressure drop across glass frit*, no soil sample

Gas Flow (nitrogen) ml/min	Pressure Drop, mm Hg	
	RT	150 C
200	14	19
400	28	39
600	40	62
800	56	80

Pressure drop across glass frit* and 30g sample of soil (-200 mesh)

Gas Flow ml/min	Pressure Drop, mm Hg		Height of soil at RT, mm
	RT	150 C	
0	0	0	41
200	16	21	50
400	29	41	50
600	42	65	52
800	57	90	70-110

*Glass frit D 32 mm, thickness 2 mm, porosity: fine (4-6 microns)

Preliminary feasibility studies of soil decontamination by gaseous extraction have been restricted to removal of arsenic and mercury from the soils. No attempts have been made as yet to demonstrate the feasibility of extracting commercial by-products.

The best result achieved up-to-date was removal of more than 99 percent of mercury, down to a level of 0.2 ppm and removal of about 70 percent of arsenic down to the level below 14 ppm (Table 6).

Classification of Soils by Gas Elutriation. The fine clay and humus particles of the soil exhibit much higher retention capacity for mercury and arsenic contaminants than do the coarser soil components. This leads to an idea of separation of the contaminated soil into two fractions, according to a certain size. The fraction finer than the selected size might contain only negligible amounts of the contaminants. Only the finer fraction of the soil would necessitate decontamination. In result, the amount of soil subject to decontamination procedure could be considerably reduced.

The correctness of this concept was checked by separation of a sample of the Army soil (30.0 grams) into two fractions by gas elutriation method. Calculations based on the Stoke's law showed that using an 18 mm tube and an air or nitrogen gas flow 20 cu.ft/hour, a separation could be achieved along an approximate particle size 44 microns, corresponding to 325 mesh sieve. Separation experiments showed enrichment of finer fraction in As and Hg content (Table 7). The departure of closure from 100 percent at least partially may be attributed to losses of As and Hg during blowing of the soil with gas. The coarser fraction contains less contaminants than the original soil, but too much for setting aside its decontamination processing. It is clear that the cut-off particle size should be much higher than 44 microns, probably between 100 and 200 microns. Separation of particles of the latter sizes by air elutriation is impractical. Further studies on this line might be performed using mechanical screening.

TABLE 6

FEASIBILITY STUDIES ON DECONTAMINATION OF SOILS BY GASEOUS EXTRACTION

Experiment	Soil Sample		Gas Mixture						Extraction		Evacuation		Concentration of Arsenic (ppm)			Concentration of Mercury (ppm)		
	Source of Soil	Particle Size Mesh	Flow ml/min	N_2 %	HCl %	H_2 %	Cl_2 %	CH_3Cl %	Temperature C	Time hrs	Temperature C	Time hrs	Before	After	% Removed	Before	After	% Removed
1	Agriculture Soil Etzkorn	-200	560	71.4	28.6	-	-	-	150	1/2	-	-	385	335	13.0	-	-	-
2		-200	560	61.4	28.6	10.0	-	-	150	1/2	-	-	385	260	32.5	-	-	-
3		-200	560	66.4	28.6	-	5.0	-	150	1/2	-	-	385	358	7.0	-	-	-
4		-200	560	61.4	28.6	5.0	5.0	-	150	1/2	-	-	385	356	7.5	-	-	-
5		-200	432	50.0	37.1	12.9	-	-	200	1/2	-	-	385	190	50.7	-	-	-
6	Rocky Mountain Soil from Army Arsenal Basin A	-200	666	67.6	24.0	8.4	-	-	200	1/2	200	1/2	40	26	35.0	39	6.	84.5
7		-200	600	100	-	-	-	-	200	1/2	-	-	40	40	0	39	23.	41.0
8		-200	-	-	-	-	-	-	-	-	200	1/2	40	32	20.0	39	26.	33.3
9		-200	666	67.6	24.0	8.4	-	-	250	1/2	250	1/2	40	16.5	58.7	39	0.8	98.0
10		-200	700	40.0	40.0	20.0	-	-	250	1/2	250	1/2	40	18	55.0	39	1.2	97.0
11		-200	-	-	-	-	-	-	-	-	300	1/2	40	39	2.5	39	1.2	97.0
12		-200	666	67.6	24.0	8.4	-	-	300	1/2	300	1/2	40	26	35.0	39	0.4	99.0
13		-200	660	76.6	-	24.0	-	-	300	1/6	300	1/2	40	26.7	33.3	39		
14		-200	660	51.5	48.5	-	-	-	300	1/3	-							
15		-200	666	67.6	24.0	8.4	-	-	200	1/2	300	1/2	40	26	30.0	39	0.6	98.5
16		-200	666	66.6	24.0	8.4	-	1.0	250	1/2	300	1/2	40	23.7	40.7	39	1.2	97.0
17		-200	666	65.6	24.0	8.4	-	2.0	250	1/2	300	1/2	46	15.6	67.0	59	0.2	99.8
18		-200	666	51.6	40.0	8.4	-	-	250	1/2	300	1/2	46	14.9	67.6	59	0.8	98.5
19		-200	666	52.0	48.0	-	-	-	250	1/2	300	1/2	46	20.6	44.8	59	0.2	99.8
20		-200	666	50.0	48.0	-	2.0	-	250	1/2	300	1/2	46	13.7	70.3	59	0.2	99.8

TABLE 7

SEPARATION OF ARMY SOIL BY NITROGEN ELUTRIATION

	Total wt %	As	Hg
Soil as received	100	40 ppm	37 ppm
Fraction +44 microns	73.3	12 ppm	16 ppm
Fraction -44 microns	26.7	44 ppm	53 ppm
Closure *, %	--	52	70

*Contaminants found in both fraction as percentage of their respective amounts in the soil before elutriation.

5. Technical Plan

Classification and Selective Grinding. When the soil is separated into two fractions according to particle size, the finer fraction is enriched and the coarser fraction impoverished in the content of mercury and arsenic contaminants. Classification according to a pre-set particle size and selective grinding for diminuting the arsenic and mercury compounds, but not the rock particles, may allow reducing the tonnage of the soil subject to gaseous extraction. Soil will be first divided into two classes using certain mesh size, for example, 100 (corresponding particle size 149 microns). This fraction will contain coarse and hard rocky particles. If the +100 mesh fraction will contain only negligible amounts of Hg and As, it will be returned to the soil without decontamination. However, if the amount of Hg and As will be excessive, this fraction will be ground selectively and classified again. The finer fraction of the soil (in the example -100 mesh) combined with the undersize fraction from grinding, will be decontaminated.

This portion of the proposed study will aim at optimizing the cut-off of the particle for classification and the method of selective grinding. The latter will include search for a proper hardness grinding medium and time of grinding.

Optimization of Process Variables. These studies will include finding optimum conditions for the decontamination process. The following variables will be studied in detail:

(1) Gas composition

(2) Temperature

(3) Time

(4) Effect of particle size

(5) Effect of moisture in the soil

(6) Effect of compounds with methyl group such as methanol or methyl chloride on the volatilization of mercury and arsenic compounds.

The gas extraction method carries the option of producing saleable by-products. It is possible to recover practically all mercury from the mercury contaminants, extract titania from the soil and convert it into commercial titanium oxide pigment and also to produce some amounts of phosgene. The feasibility study of the "commercial" version of the decontamination process may be studied also. It will include optimal conditions for simultaneous conversion of arsenic, mercury and titanium compounds into their volatile chloride, as well as the reaction of formation of phosgene by reaction of iron chlorides with hot air and carbonaceous organic matter from the soil.

Upscaling the Process and Conversion to Continuous Operation. After completion of laboratory optimization studies, the process will be evaluated in detail from a technological and economical point of view. Detailed flow diagram, material and energy balances will be worked out. Upscaling the process in the laboratory for decontamination of 5 lb of soil per hour will be combined with recirculating of the reacting gases and conversion of the process into a continuous or semicontinuous operation.

6. Implementation of the Program

Implementation of the program, divided into specific tasks, is presented on the following page (Table 8).

TABLE 8
PROGRAM IMPLEMENTATION

Classification	Month 1	2	3	4	5	6	7	8	9	10	11	12
Selective Grinding	→	→	→	→								
Optimization												
Gas Composition	→	→	→	→	→	→						
Temperature	→	→	→	→	→	→						
Time	→	→	→	→	→	→						
Particle Size for Fluidization	→	→	→	→	→	→						
Water Content	→	→	→	→	→	→						
Effect of Methyl Group	→	→	→	→	→	→						
Commercial Version												
Effect of Gas Composition and Temperature on the Yield of $TiCl_4$				→	→	→	→	→	→	→		
Optimum Conditions for Formation of Phosgene				→	→	→	→	→	→	→		
Evaluation Studies												
Technological								→	→	→	→	→
Flow Sheet								→	→	→	→	→
Material Balance								→	→	→	→	→
Thermal Balance								→	→	→	→	→
Economical Evaluation								→	→	→	→	→

7. Manpower Requirement

The activity outlined in the previous sections is anticipated to require two man years of technical effort over a one year period. The estimated cost is $100,000. If the results of the laboratory efforts justify further work, a Phase II pilot scale program at the four man years, $200,000 level should be funded. This would be followed by a demonstration program requiring approximately $500,000.

ISOLATION OF MERCURY AND OTHER HAZARDOUS HEAVY METALS FROM DILUTE WASTE STREAMS

1. Introduction

Governmental legislation restricting the amount of hazardous waste industry may discharge into the environment presents a singular challenge to technology; that is to provide the means whereby industry may be responsive to such legislation on the one hand, and on the other hand, minimize the cost of the products it manufactures.

The cost restriction disallows many of the techniques and processes relative to hazardous waste isolation and passivation developed to date. Low cost processes are required, particularly in respect to heavy metal contaminants. These contaminants stem for the most part from industrial operations which yield relatively inexpensive products such as power, plated materials, insecticides, herbicides, etc. No significant increase is allowable in the price of such products.

It is the purpose of this section to present efficient, low cost vehicles for isolating heavy metals from aqueous waste streams. The heavy metal isolation technology is formulated with the view of providing processes potentially lower in cost than those processes comprising the present technology. Furthermore, the technology is designed to specifically remove hazardous heavy metals from aqueous waste streams while minimizing interaction with other stream components.

This section shows sulfur and its polymeric compounds as the preferred vehicles for isolating heavy metals from water. Selected sulfur compositions are described and the pertinent technical literature is reviewed with respect to showing the chemical versatility of these compositions. The selected sulfur compositions are related to various isolation techniques. Experimental work at TRW Systems showed how sulfur compositions could be tailored to

increase the effectiveness of heavy metal isolation from water by filtration and by extraction. The recommended future work is designed to yield additional sulfur compositions for use as efficient, low cost vehicles in isolating metal contaminants.

2. Technical Approach

The isolation of contaminants and their passivation (discussed elsewhere in this volume) is the key to the decontamination of heavy metal containing aqueous streams. Ideally, mercury and other hazardous heavy metals in aqueous waste streams should be isolated in as pure a form as possible since the low amount of material gives lowest cost in the process selected for their passivation prior to ultimate disposal. However, reduction of the contaminant to the minimal quantity may lead to increased isolation costs; therefore, tradeoff may be required to minimize overall disposal costs. A major factor in the cost analysis is the cost of the materials used to separate the heavy metal.

Sulfur and its polymeric compounds are proposed as key materials for separation of heavy metal contaminants from water because they are very low in cost and chemically versatile. Their potential ability to reduce heavy metal contaminants in aqueous streams to extremely low concentrations is particularly important. Furthermore, the costs of these materials is expected to decrease in the future since the products of desulfurization of coal, oil and other fuels are sulfur compounds. As fossil fuel desulfurization becomes more practical the compounds will be produced in increasing amounts.

Sulfur and its polymeric compounds can be used to separate heavy metals such as mercury, arsenic, chromium, lead, selenium, cadmium, and beryllium from a dilute aqueous environment. This separation can be carried out by employing one of three isolation operations: (1) flocculation, (2) ion exchange, or (3) extraction.

The technical approach is designed to designate or tailor sulfur and its polymeric compounds for each of the three isolation techniques. With

these operations in hand, one can address the method deemed appropriate for decontamination in light of the chemical and physical make-up of the aqueous stream under consideration, thus providing general applicability.

Sulfur and its Polymeric Compounds. The classes of composition of sulfur recommended for study are sulfhydryls and polymeric sulfurs bearing chemically functional groups. Some of the sulfhydryls are designed to bear acidic functional groups in addition to mercaptan groups. Certain sulfur compositions bear either weak or strong acid groups, the former being carboxylic and the latter being sulphonic. Others bear negatively charged sulfur with sodium counterions. The role of the polymeric sulfur, in addition to its inherent ability to sequester heavy metals in aqueous streams, is to fashion metal complexes that are applicable to the selected isolation operation. Thus in flocculation, for example, the size of the insoluble suspensoids fashioned upon formation of metal complexes is tailored by polymeric sulfur to make flocculation efficient. In extraction, polymeric sulfur renders the metal complexes soluble in non-polar solvents. And in ion exchange, it disperses the functional groups so that maximum contact is effected with the aqueous environment.

Sulfhydryl Compounds with S_x Moieties. Fanelli[1] showed that upon passing of hydrogen sulfide (H_2S) through molten sulfur at 160 to 390 C the viscosity of the melt is reduced by as much as one thousandfold. In this case H_2S acts as chain stopper as follows:

$$H_2S + S_x \rightarrow HS - S_{x-1} - SH \qquad (1)$$

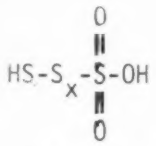
In reaction 1, the mercaptan groups (-SH) which render heavy metals highly water insoluble are bound by low cost sulfur atoms. Here H_2S, a gas which also readily precipitates heavy metals from aqueous solution, is chemically "fixed" by sulfur. The resulting non-gaseous compounds are applied to aqueous streams more conveniently than the hazardous gas, H_2S. Furthermore, tailoring the sulfhydryl compounds by varying their molecular weights provides a means whereby the precipitant may be designed for most effective flocculation.

Other reactions valuable in providing materials for the flocculation operation are the reactions of sulfur with aqueous sodium hydroxide at 100 C which yield sodium polysulphides as follows:[2]

$$S_x \xrightarrow{NaOH} NaS - S_{x-2} - SNa \qquad (2)$$

Reaction 2 products may be employed as such as precipitants for heavy metals, or they may be "cracked" by heating at pressures of 10 to 15 mm Hg to yield a mixture containing H_2S_2, H_2S_3, and H_3S_4,[3,4] these latter compounds containing the desirable mercaptan groups.

Of particular interest in this study are the sulfane monosulphonic acids.



Sulphane Monosulphonic Acid

The sulfonic acid group is hydrophilic in contrast to the sulfane portion of the molecule which is hydrophobic. Such materials form stable dispersions in water; and the small size of the dispersoids, approximately colloidal dimensions, makes a large area of material available for interaction with metal contaminants. Dispersions may also be formed through utilization of alkaline metal salts of sulphane monosulphonic acids.

Sulphane monosulphonic acids provide the mercaptan groups for reaction with metal contaminants in an aqueous environment. Particularly important, in our opinion, are the high sulfur containing compounds since the mercaptan groups stemming from higher molecular weight compounds of reaction 1 are not as readily available for interaction because these compounds tend to be increasingly hydrophobic with increasing molecular weights. Furthermore, the strong acidic nature of these sulphane monosulphonic acids allows stable dispersions in acidic as well as basic aqueous waste streams.

A ready method for the preparation of sulphane monosulphonic acids was given by Schmidt.[5] Treating sulphanes (such as those prepared by reaction 1) at low temperatures in ether with sulfur trioxide yields sulphane monosulphonic acids as follows:

$$HS - S_{x-1} - SH + SO_3 \rightarrow HS - S_x - SO_3H \qquad (3)$$

Another source of sulphanes for reaction with sulfur trioxide as shown in reaction 3 are the aforementioned "cracking" reactions of sodium polysulphides.

Polymeric Sulfur as Electron Donors. The salts of many heavy metals form additional compounds with electron donor molecules, and polymeric sulfurs are strong electron donors. Such materials provide an advantage in heavy metal decontaminantion processes, heavy metals are more readily separated chemically from sulfur compounds without mercaptan groups than from those containing such groups. Furthermore, when required, they offer the potential of isolating contaminant metals without affecting noncontaminant ones such as calcium. Polymeric sulfurs fashion insoluble complexes with heavy metals in the presence of alkaline earth metals and leave the latter unprecipitated due to the absence of sulfhydryl compositions.

Of particular interest is polymeric sulfur containing the carboxyl group and sulphonic acid group because these groups facilitate the formation of dispersions in water. Carboxyl containing sulphanes are realized through the interaction of free radicals with elemental sulfur at 112 C[6,7] as follows:

$$HOOC\text{-}RN_2R\text{-}COOH + S_x \rightarrow HOOC\text{-}R\text{-}S_x\text{-}R\text{-}COOH + S_x\text{-}R\text{-}COOH \qquad (4)$$

The free radicals are intermediate products of reaction 4 produced as follows:

$$HOOC\text{-}RN_2R\text{-}COOH \rightarrow \cdot R\ COOH + N_2 \uparrow \qquad (5)$$

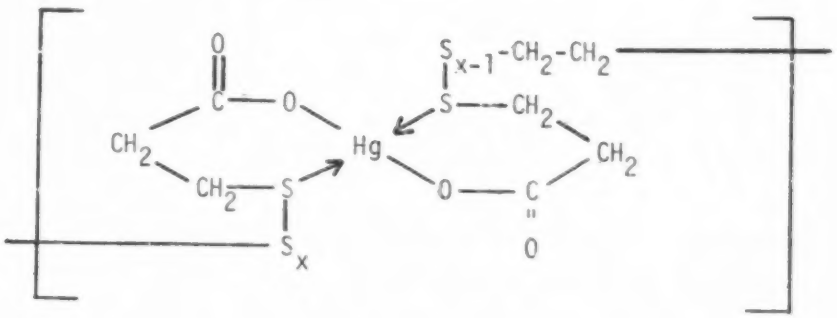
The free radicals formed in reaction 5 react with elemental sulfur to give the products shown in reaction 4.

Sulphane disulphonic acids are prepared as follows:[8]

$$H_2S + SO_2 \xrightarrow[\text{Acetic Acid}]{\text{50\% Aqueous}} HO\text{-}\overset{\overset{O}{\|}}{S}\text{-}S_x\text{-}\overset{\overset{O}{\|}}{S}\text{-}OH \qquad (6)$$

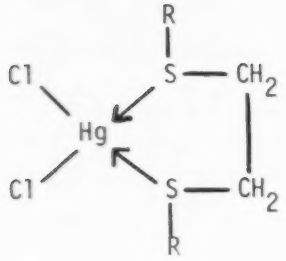
Thus by employing reactions 4 and 6 polymeric sulfur bearing weak and strong acid groups are realized. By these means it is possible to tailor dispersions and precipitants relative to the isolation operation.

The heavy metal sequestering power of polymeric sulfur is exemplified by the reaction between Hg^{++} ions and $HOOCH_2CH_2S_xCH_2CH_2COOH$ to yield $[OOCCH_2CH_2S_xCH_2CH_2COOHg]_n$, which in turn forms an intramolecular chelate idealized as follows:



Such compounds render heavy metals amenable to isolation from aqueous waste streams by either extraction or flocculation operations because: (1) their covalent character promotes solubility in organic solvents, and (2) their precipitants are hydrophobic which promotes separation from aqueous environments.

The electron donor portion of sulfur which contains carboxyl or sulfonic acid groups resides in the sulfur atoms. Mercury chloride, for example, is known to complex with thio ethers to yield compounds of the following type:



Flocculation Operation. Flocculation is an isolation operation wherein insoluble contaminants suspended in a liquid matrix are made to consolidate and settle. The decontaminated liquid is siphoned off. This operation is widely employed in municipal and industrial water clarification processes. With suitable, cheap materials for rendering soluble heavy metals amenable for flocculation, this operation is an attractive means for the decontamination of aqueous waste streams containing heavy metals.

To provide information about mercury containing suspensoids amenable to flocculation, the proof-of-principle experimental studies carried out at TRW included an investigation of degree of heavy metal consolidation effected employing sulfur compositions as a function of several reaction variables. The objective was the formation of large particles containing mercury with a very low concentration of the contaminant reamining in the aqueous environment. Large particles are desired in order to effect efficient flocculation.

Sulfhydryl Ion Exchange Materials. Ion exchange materials cause the isolation of chemical species by the release of expendible ones. Such materials are effective in decontamination of heavy metal containing aqueous waste streams, involving the expenditure of non-hazardous metals for hazardous ones. In this respect ion exchange resins are well known, and in a recent work silicon alloys were employed in place of resins for the removal of heavy metals from water and brine.[9]

TRW proposes modified sulfur and its polymeric compounds as ion exchange resins for decontamination of aqueous streams containing heavy metals. Sulfhydryl ion exchange materials may be prepared by the

addition of hydrogen sulfide to polyunsaturated olefinic resins. Such additions are facilitated by catalysts, among which are clay,[10] metallic sulfides,[11] and sulfur.[12] Of particular interest in our study are materials stemming from the addition of hydrogen sulfide to polybutadienes in the presence of sulfur. The ion exchange materials fashioned will contain a varied multiplicity of alkyl mercapto, polysulfomercapto and sulphane groups that have unusual affinity, as described previously, for heavy metals in aqueous solution. In addition, these materials can be fashioned as low density foams having dimensional integrity, offering maximum exposure of functional groups to an aqueous environment and capability for mechanical withdrawal from that environment.

Extraction Operation. For extraction, heavy metal complexes are formed by the heavy metal contaminants with selected sulfur compounds. Such complexes may be soluble in water or insoluble; they are, however, designed for maximum solubility in organic liquids such as benzene, toluene, xylene, kerosine, etc. This solubility in organic liquids which are nonmiscible with water permits the extraction of heavy metal contaminants from an aqueous matrix by organic liquids.

Mercaptans were selected for TRW proof-of-principle experiments as the model compounds with which the extraction operation may be carried out. The reaction of a mercaptan or thiophenol with aqueous solutions of salts of heavy metals gives highly insoluble mercaptides. The insoluble compounds of mercury, lead, zinc, and copper have been previously synthesized and studied.[13] The reaction of a heavy metal salt, e.g., lead, salt, with a mercaptan occurs as follows:

$$2RSH + (CH_3COO)_2\,Pb \rightarrow Pb(SR)_2 + 2CH_3COOH \qquad (7)$$

The heavy metal mercaptides produced in reaction 7 are highly insoluble in water due to the covalent nature of the heavy metal-sulfur bond and the alkyl groups, R. The latter can be tailored to further promote the insolubility of these compounds in aqueous matrices. Fortunately, the above parameters causing water insolubility on the other hand, are those which

promote, on the other hand, dissolution in organic liquids. Tailoring the extent of solubility of these compounds in organic liquids may be carried out by varying the nature of the R groups.

Although the TRW proof-of-principle experimental study included investigation of the above process employing R groups of alkyl compositions, the final objective is to replace alkyl compositions with S_x ones. Tailoring of S_x groups to make extraction operations possible will follow experimental observations concerning extractability of heavy metal alkyl mercaptans by non-polar solvents in an aqueous environment.

3. Proof-of-Principle Experimentation

One objective of this study was to determine whether S_x anions are employable in reducing the mercury content of aqueous waste streams to values less than 10 ppb. Although heavy metal sulfides are known to be generally very nonsoluble in water, this knowledge is at best only indicative of the sequestering power of S_x ions. The determination of the solubility of heavy metal sulfides per se does not indicate whether these compounds readily consolidate in an aqueous matrix in a manner amenable to isolation operations. In the absence of such compound consolidation, isolation operations, such as filtration and flocculation, cannot be carried out efficiently. In other words, sequestered heavy metals must be tailored to the isolation operation employed in order to realize effective decontamination. In the proof-of-principle studies filtration through filter paper was investigated to simulate flocculation operation.

Mercury Flocculation Study. S_x ions were employed in the precipitation of mercury from aqueous solutions of mercuric chloride ($HgCl_2$) at .001M (201 ppm Hg) and .01M (2010 ppm Hg). The precipitants were formed by mixing with sodium polysulfide solutions to yield mixtures of pH 8. Precipitations were also carried out in the presence of ammonium chloride. The resulting cloudy, grey mixtures were filtered through Whatman Filter Paper No. 42. The aqueous effluents were mixed with a stannous chloride solution, a reducing solution for mercury cations, producing elemental mercury whose concentration was determined by flameless Atomic Absorption Technique.

Table 1 gives the results of these determinations in respect to the above procedure.

No apparent mercury appears in the aqueous effluents (Table 1), however, examination of the filter papers showed essentially no retention of solidus matter from mixtures resulting from the .001M solutions. These observations indicated that mercury indeed existed in the aqueous effluents but in a state non-reducible by the stannous chloride solution, explaining the essential absence of mercury indicated by absorption analysis. In order to render the aqueous effluents amenable to analysis by Atomic Absorption they were treated with permanganate solution producing mercury cations. These effluents were then reduced by stannous chloride.

The initial concentration of mercuric chloride solutions was found to determine whether the resulting precipitants consolidated sufficiently to be effectively isolated by the filter paper employed (Table 2). The more effective decontamination was obtained through precipitation of the more concentrated solution, i.e., 2010 ppm Hg. Furthermore, the results (Table 2 combined with those of Table 1) show that essentially all the precipitated mercury which persists in the aqueous effluent does not exist in the cationic state.

Observations of color and/or particles in the aqueous effluents indicated that extraneous dissolved and dispersed matter existed in the aqueous effluents. Combining these observations and the results (Table 1 and 2) leads to the conclusion that both the dissolved matter and the dispersed matter within the water contained mercury, and that the mercury existed in a chemical complex bearing a negative charge. This conclusion explains the non-consolidation of the dispersed mercury, and its non-formation of elemental mercury upon treatment with reducing solution.

Nonfilterable mercury in aqueous effluents from S_x precipitation, therefore, was postulated to exist as negative charge complexes in the physical state of dissolution and dispersion. Since the charge stabilized the dispersion of mercury in the aqueous matrix, neutralization of this

TABLE 1

MERCURY CATIONS REMAINING IN WATER FOLLOWING PRECIPITATION BY VARIOUS POLYSULFUR ANIONS

Hg Concen. in Water, ppm \ Precipitating Anion*	Concentration of Hg in Aqueous Effluent, ppm			
	$S_{1.2}^{=}$	$S_{1.3}^{=}$	$S_{1.4}^{=}$	$S_{1.5}^{=}$
201	<.01[§]	<.01	<.01	<.01
2010	<.01	<.01	<.01	.04
201[†]	.01	<.01	.04	<.01
2010[‡]	<.01	.01	.01	<.01

*Postulated composition stemming from the amount of elemental sulfur dissolved in caustic yielding sodium polysulfide solution.

[†]Residing in the presence of 0.001 M NH_4Cl.

[‡]Residing in the presence of 0.01 M NH_4Cl.

[§]An absolute value below the analytical sensitivity of flameless atomic absorption.

TABLE 2

MERCURY DECONTAMINATION EFFECTIVENESS OF VARIOUS POLYSULFUR ANIONS IN RESPECT TO INITIAL CONCENTRATION OF CONTAMINANT

Hg Concen. in Water, ppm \ Precipitating Anion*	Concentration of Hg in Aqueous Effluent, ppm		
	$S_{1.2}^{=}$	$S_{1.3}^{=}$	$S_{1.4}^{=}$
201	166	-	55
2010	6	-	3.2
201†	-	108	150
2010‡	-	1.0	1.0

*Postulated composition stemming from the amount of elemental sulfur dissolved in caustic yielding sodium polysulfide solution.

†Residing in the presence of 0.001 M NH_4Cl.

‡Residing in the presence of 0.01 M NH_4Cl.

charge should effect additional mercury consolidation. Consequently, polyvalent cations stemming from low cost compounds were screened. In this particular case, calcium chloride was found to be an efficient consolidating agent for nonfilterable mercury.

The above described procedure was found to be very effective (Table 3). These results upon comparison of the results in Table 2 show that further decontamination was carried out by neutralization of the negative charge complexes. It was accomplished, essentially, by more effective consolidation of the dispersed mercury in the aqueous effluents. The formation of particles can be observed visually. Figure 1 provides a photographic rendition of the phenomena yielding results given in Table 2 and 3.

By allowing the consolidation of dispersed mercury by calcium chloride to occur in the presence of dispersed matter Nuchar-C-19-14, in the aqueous matrix, very effective decontamination was realized (Table 4). Employing the $S^{=}_{1.4}$ ppt. ions, (the value of 1.4 obtained adding elemental sulfur to Na_2S) the resulting aqueous effluent is estimated to contain less than 10 ppb of mercury. Nuchar-C-190-14 was found to also separate mercury from water, however, even with extensive treatment, the mercury content of the water did not fall to a value less than 0.56 ppm.

Mercury Extraction Study. A further objective of the proof-of-principle study was determination of the chemical compositions containing sulfur which facilitate separation of mercury from water by the extraction operation. The materials employed in producing mercury complexes which are extractable from water by organic liquids were commercially available mercaptans from Industrial Chemicals Division, Pennsalt Chemical Corporation.

Selected for investigation in this study were three materials:

(1) n-butyl mercaptan

$CH_2CH_2CH_2CH_2SH$

(2) n-octyl mercaptan

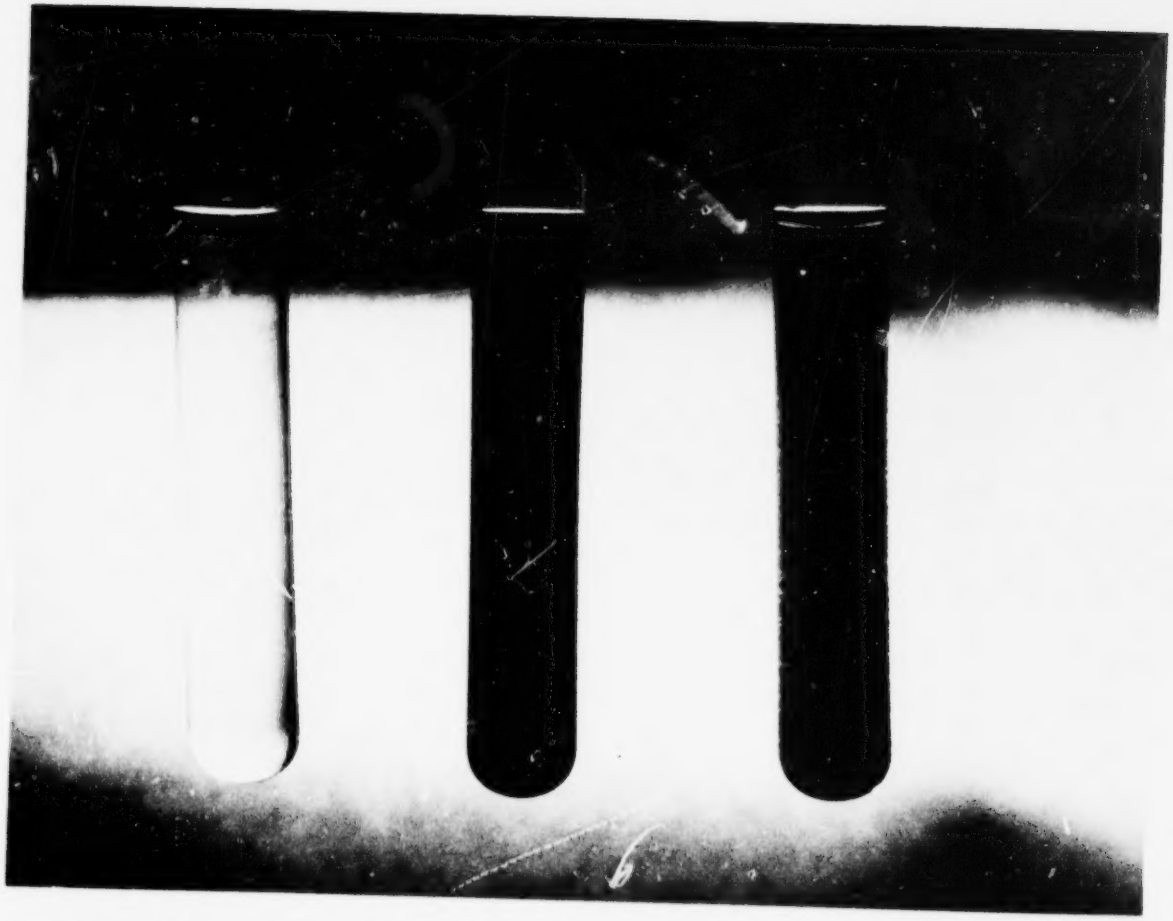
$CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ SH$

TABLE 3

DECONTAMINATION EFFECT OF CALCIUM IONS

Hg Concen. in Water, ppm \ Precipitating Anion*	Concentration of Hg in Aqueous Effluent, ppm	
	$S_{1.2}^{=}$	$S_{1.4}^{=}$
201	2.40	0.32

*Postulated composition stemming from the amount of elemental sulfur dissolved in caustic yielding sodium polysulfide solution.



Aqueous solution of 201 ppm Hg

Dispersion fashioned with sodium polysulfide

Coagulation resulting from calcium chloride

Figure 1. Nature of dispersion of mercury in water with sequential addition of sulfur anions and calcium cations.

TABLE 4

DECONTAMINATION EFFECT OF CALCIUM IONS
IN THE PRESENCE OF CALCIUM BLACK

Hg Concen. in Water, ppm \ Precipitating Anion*	Concentration of Hg in Aqueous Effluent, ppm	
	$S_{1.2}^{=}$	$S_{1.4}^{=}$
201	.01	<.01

*Postulated composition stemming from the amount of elemental sulfur dissolved in caustic yielding sodium polysulfide solution.

(3) n-amyl mercaptan

$CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ SH$

The organic liquids used to extract the metal complexes can be renewed by distillation, cooled to precipitate the complex, or extracted of the heavy metal by an aqueous acidic solution as follows:

$$Hg(SR)_2 + HCl \rightarrow 2RSH + HgCl_2$$

In the last method the metal is released from the complex and dissolves into the aqueous phase. The sulfur bearing moiety of the complex remains within the organic liquid, and it is active for further heavy metal isolation.

About 20 cc of .001M mercury acetate solutions (201 ppm Hg) were treated with the above mercaptans, and extractions of the resulting precipitants dispersed in the aqueous environment were carried out with an equal volume of toluene. The mixture was hand shaken, allowed to settle in a separatory funnel, and the bottom aqueous layer was drawn off.

Visual observation of the aqueous effluents showed that sparkling clear water was obtained when n-butyl mercaptan was employed. Neither of the other two mercaptans, n-octyl mercaptan and n-amyl mercaptan produce a clear product. Analysis of the aqueous phase of the n-butyl mercaptan system demonstration that mercury concentration was reduced to a value of .01 ppm.

The above method was repeated employing mercury chloride in place of mercury acetate to determine whether the method was equally effective for heavy metal salts of strong acids as it was for those of weak acid. It was found that the method was equally effective in both cases.

Conclusions from Proof-of-Principle Experimentation. The experimental work at TRW leads to certain conclusions concerning the sequestering of heavy metal contaminants in dilute aqueous waste streams. As observed by other workers, sulfide anions per se were found to be not capable of reducing the mercury content of water to very low values, i.e., 10 ppb. It

is postulated that this is due to the drift to basicity which the aqueous solution undergoes upon addition of alkaline metal sulfides to water in amounts sufficient to realize stoichiometric equivalence vis-a-vis heavy metal contaminants. At this point, the contaminants are incorporated into negative charge complexes. In contrast to the cationic state of the contaminants, these complexes remain dispersed in water in the presence of additional sulfide ions.

The extent of cationic mercury in the water converted into negative charge complexes was found to depend upon the initial concentration of the contaminant in the aqueous matrix. The more concentrated solutions were found to yield precipitates of larger size, and these larger particles were more resistant to dispersion by a basic aqueous matrix. Consequently, significantly higher conversion of cationic contaminants into negative charge complexes occur in the more dilute solutions. Indeed as Table 2 shows concerning the 201 ppm Hg solution, practically all of the mercury was converted, whereas for the 2010 ppm Hg the extent of conversion was nil. Notwithstanding the more efficient separation of mercury from increasingly concentrated aqueous solutions, water was not decontaminated to the extent that it was free (less than 10 ppb) of heavy metal.

A significant conclusion of the TRW proof-of-principle experimentation is that the efficiency of coagulating the negative charge complexes through the use of polyvalent cations depends upon the amount of sulfur in the complex. This conclusion will be instrumental for defining future work in the sequestering of heavy metal contaminants in dilute aqueous streams. Specifically, it suggests a study providing detailed definition of sulfur compositions and polyvalent cations which, on the one hand, will aggregate heavy metal contaminants in dilute aqueous solutions into large insoluble particles, such particles being amenable to ready isolation. The aqueous stream, on the other hand, is left free of heavy metal contamination.

The TRW proof-of-principle experimentation showed that the extraction of mercury in water by organic liquids is more effective when the lower molecular weight alkyl mercaptans are employed. This is believed due to the greater miscibility in water of the lower molecular weight mercaptans.

Despite greater hydrophilicity of the lower molecular weight compounds the resulting mercapto-mercury complexes were extracted easily by organic liquids. This result leads to the conclusion that the preparations of Finelli,[1] $HS-S_{x-1}-SH$ and those preparations stemming from the "cracking" of sodium polysulphides[5,6] are polymeric sulfur compositions potentially valuable for use in extraction of heavy metals from water by non-polar liquids because in these preparations, polymeric sulfurs are obtained in the low molecular weight range.

4. Recommended Future Work

The proof-of-principle studies, including review of literature concerning sulfur chemistry applicable to sequestering heavy metals in an aqueous environment, and the experimental work provided information showing the validity of the concept of employing polymeric sulfur for efficient heavy metal separation from water. The objective of further work is to define the chemical parameters and the reaction variables for polymeric sulfur, aqueous heavy metal systems important to three isolation operations; flocculation, ion exchange, and extraction. Realization of this objective will provide the means for tailoring the reaction systems specifically to the purification of a great variety of heavy metal containing aqueous effluents. The purpose of the proposed effort is to reduce the heavy metal content of aqueous waste streams to a value less than 10 ppb at low cost.

TRW recommends that work in the immediate future consists of three tasks each concentrating on a class of sulfur system providing properties necessary to the three separation operations.

Task I concentrates on the polymeric system containing both mercaptan groups and a negative charge. The proposed effort is a continuation of the work previously described. Its objective is to define and produce chemical systems stemming from polymeric sulfur compositions and attendant chemical compositions which make flocculation and extraction operations effective in separating heavy metals from water. The chemical systems will be designated to meet the requirements of present flocculation operations employed commercially.

Task II involves the investigation of additional polymeric sulfur compositions (mercapto and acidic groups containing polymeric sulfur) in a manner analogous to Task I. Its objective is the definition and preparation of chemical systems containing polymeric sulfur which sequesters heavy metals in water under conditions not conducive to the utilization of Task I materials, such as strongly acidic aqueous streams. The acidic groups of materials to be studied are limited to the sulphonic acid and carboxylic acid types.

Task III is the synthesis of materials positioning the chemical groups of Task I and Task II onto a carrier in an arrangement capable of being submerged and withdrawn from water. These materials can function as ion exchange resins providing an alternative operation to flocculation and liquid-liquid extraction. One of the objectives of this task is the preparation of ion exchange resins which are lighter than water, dimensionally stable foams having a high surface area. With such materials a solid-liquid extraction operation may be feasible in contrast to the liquid-liquid extraction utilized in TRW's proof-of-principle experimentation. In batch operation the heavy metal contaminated water would agitate with the foamed ion exchange resins which would float to the surface and be removed by skimming. The collection of the resin can be readily carried out by methods now employed in cleaning oil slicks from the surface of water.

5. Manpower and Schedule Requirements

It is estimated that the recommended three-task program of laboratory research can be completed within a time frame of 12 to 18 months at a cost of $150,000 to $200,000. Successful laboratory demonstration of polysulfide materials would be followed by bench-scale and pilot plant evaluations of the best sequestering materials with actual waste streams.

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A NEW PROCESS FOR THE ECONOMIC UTILIZATION OF THE SOLID WASTE EFFLUENT FROM LIMESTONE SLURRY WET SCRUBBER SYSTEMS

1. Problem Background

Over 60 billion lb of sulfur oxides are emitted yearly into the atmosphere in the United States and of this total, 60 percent of the oxides of sulfur come from coal fired power plants. At the present time limestone slurry wet scrubbing systems for removing sulfur oxides from power plant stack gases have advanced to major pilot plant and full scale demonstration stages. Although these systems are promising for controlling the power plant sulfur oxide air pollution problem they, in turn, also have the potential of creating a major solid waste pollution problem. Namely, for a typical 1,000 MW wet scrubbed power plant, some 1,300 tons/day of calcium sulfate-calcium sulfite-fly ash solid waste are produced.

A second problem, seemingly unrelated to sulfur oxide pollution, involves the current dependence of the U.S. alumina (Al_2O_3) and aluminum industries on the importation of foreign ores. Over 85 percent of the ores (e.g., bauxite) used in the U.S. production of alumina (and ultimately aluminum) are currently imported and hence are subject to the political influences of foreign countries. Extraction of alumina from abundant low grade domestic ores such as clay ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) have been extensively evaluated at the bench-scale and pilot plant level. However, at the present time these processes (such as the Bureau of Mines lime-soda sinter process) fall just short of being economically competitive with the Bayer processing of imported bauxite.

2. Recommended Problem Solution

TRW has recently conceived a processing scheme which addresses itself to the solution of both the above described problems. Namely, the calcium

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(or magnesium) containing waste from the sulfur oxide wet scrubbing system can be economically utilized in the extraction of alumina from low grade domestic ores (clay). The process also produces cement (calcium silicates) and sulfur. This processing scheme results in the total utilization of the wet scrubber solid waste effluent, further, the sale of the products is expected to pay the processing costs.

A simplified process flow diagram and rough material balance (Figure 1) have been prepared for a system designed to operate on the solid effluent from a wet scrubbed, 1,000 MW, coal burning power plant which produces 300 tons per day of sulfur as either calcium sulfate or calcium sulfite. Thirteen hundred tons per day of $CaSO_4$ or equivalent together with 640 tons per day of clay ($As_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), 25 tons per day of makeup sodium carbonate and 225 tons per day of recycle sodium carbonate are fed to a rotary kiln where the reactants are heated in a reducing combustion environment at 1,000 to 1,250 C. The sulfur present in the feed is converted to H_2S which is fed together with the combustion gases to a Claus type of sulfur recovery unit or possibly a TRW S-100 sulfur recovery unit. Primary reactions in the kiln result in the formation of soluble sodium aluminate ($Na_2O \cdot Al_2O_3$) and insoluble dicalcium silicate ($SiO_2 \cdot 2CaO$) thus providing the means for separating the alumina from the silica portion of the clay.

The sintered product from the kiln is leached with a dilute solution of sodium carbonate which dissolves the sodium aluminate and leaves the dicalcium silicate as an insoluble residue. The dicalcium silicate is filtered and used as a primary raw material in the manufacture of cement. Carbon dioxide is bubbled through the sodium aluminate solution resulting in the precipitation of aluminum hydroxide and the regeneration of the sodium carbonate. The aluminum hydroxide is filtered and calcined to the final alumina product. The sodium carbonate is recycled to the kiln.

Based on current raw material and product prices and assuming that calcium sulfate is free to the process; $3,210.00/day of raw materials result in $14,020.00/day of saleable products.* Therefore, rather

*Taking no credit for sulfur and only $1/ton for dicalcium silicate.

substantial operating and capital costs can be tolerated and still result in a net positive cash flow for the process.

3. Recommendations

The basic chemistry depicted (Figure 1) is well established. However the applicability of the chemistry to the new processing scheme (Figure 1) and to actual scrubber effluent material has not yet been demonstrated. It is therefore recommended that a Phase I program of bench-scale laboratory investigation and preliminary engineering design be initiated in order to determine the technical and economic potential of this recommended process. The initial program phase would be aimed at:

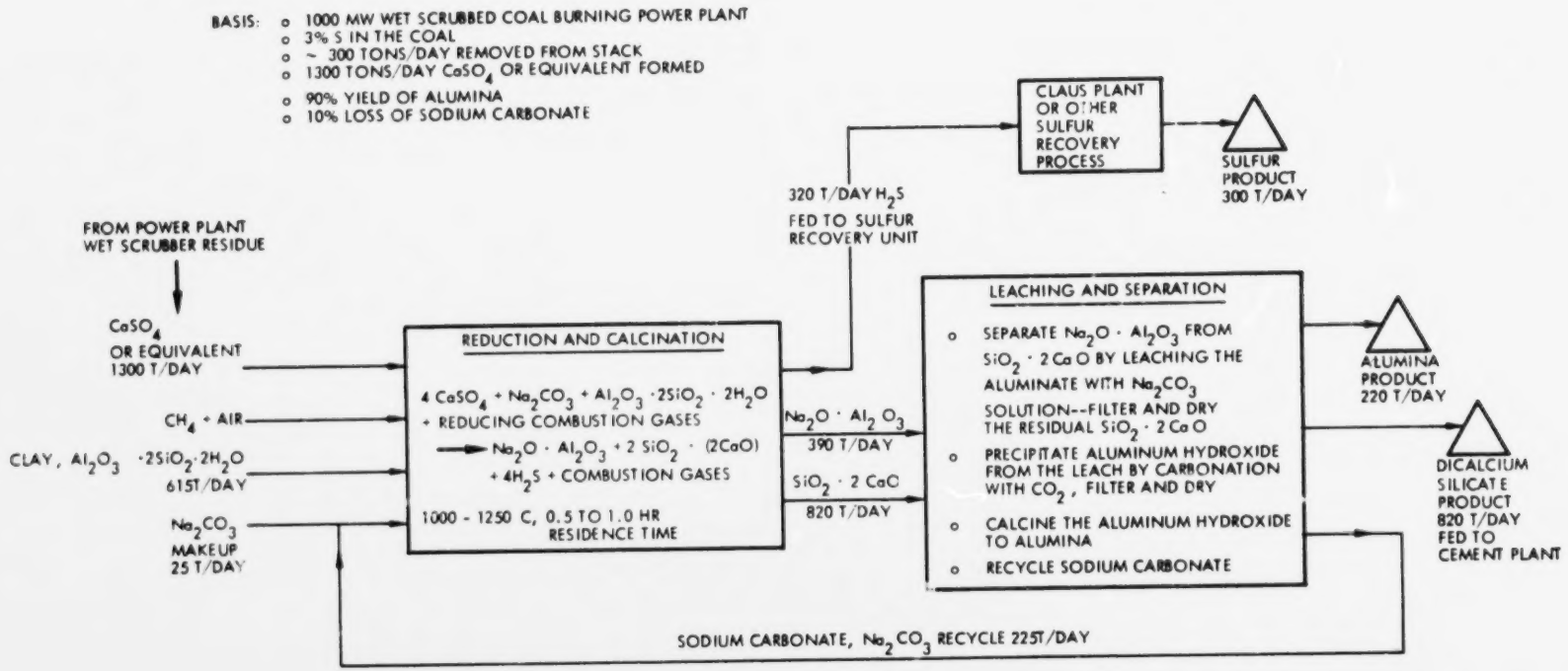
(1) determining probable ranges of operating conditions for each of the major processing steps (reduction, calcination, leaching, separation);

(2) determining (with actual scrubber effluent) probable yields and purity of products;

(3) developing a preliminary process design including material and energy balances;

(4) estimating capital and operating costs and determining the economic viability of the process.

It is estimated that the Phase I feasibility study described above can be completed within 12 months at a cost of about $150K.


BASIS:
o 1000 MW WET SCRUBBED COAL BURNING POWER PLANT
o 3% S IN THE COAL
o ~ 300 TONS/DAY REMOVED FROM STACK
o 1300 TONS/DAY $CaSO_4$ OR EQUIVALENT FORMED
o 90% YIELD OF ALUMINA
o 10% LOSS OF SODIUM CARBONATE
CLAUS PLANT OR OTHER SULFUR RECOVERY PROCESS
SULFUR PRODUCT 300 T/DAY
320 T/DAY H_2S FED TO SULFUR RECOVERY UNIT
FROM POWER PLANT WET SCRUBBER RESIDUE
$CaSO_4$ OR EQUIVALENT 1300 T/DAY
CH_4 + AIR
CLAY, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ 615T/DAY
Na_2CO_3 MAKEUP 25 T/DAY
REDUCTION AND CALCINATION
$4\,CaSO_4 + Na_2CO_3 + Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$
+ REDUCING COMBUSTION GASES
$\rightarrow Na_2O \cdot Al_2O_3 + 2\,SiO_2 \cdot (2CaO)$
$+ 4H_2S$ + COMBUSTION GASES
1000 - 1250 C, 0.5 TO 1.0 HR RESIDENCE TIME
$Na_2O \cdot Al_2O_3$ 390 T/DAY
$SiO_2 \cdot 2\,CaO$ 820 T/DAY
LEACHING AND SEPARATION
o SEPARATE $Na_2O \cdot Al_2O_3$ FROM $SiO_2 \cdot 2\,CaO$ BY LEACHING THE ALUMINATE WITH Na_2CO_3 SOLUTION--FILTER AND DRY THE RESIDUAL $SiO_2 \cdot 2\,CaO$
o PRECIPITATE ALUMINUM HYDROXIDE FROM THE LEACH BY CARBONATION WITH CO_2, FILTER AND DRY
o CALCINE THE ALUMINUM HYDROXIDE TO ALUMINA
o RECYCLE SODIUM CARBONATE
ALUMINA PRODUCT 220 T/DAY
DICALCIUM SILICATE PRODUCT 820 T/DAY FED TO CEMENT PLANT
SODIUM CARBONATE, Na_2CO_3 RECYCLE 225T/DAY

RAW MATERIAL AND PRODUCT SUMMARY

RAW MATERIALS	COST/DAY	PRODUCTS	VALUE/DAY
1. $CaSO_4$ 1300 T/DAY FREE TO PROCESS	$ 0.00	1. ALUMINA, 220 T/DAY AT $ 60/T	$ 13,200.00
2. CLAY, 615 T/DAY AT $4.00/T	$ 2460.00	2. DiCALCIUM SILICATE, 820 T/DAY AT $1/TON	$ 820.00
3. SODIUM CARBONATE, 25 T/DAY AT $ 30.00/T	$ 750.00	3. SULFUR 300 T/DAY, NO VALUE	$ 0.00
	$3210.00		$ 14,020.00

Figure 1. Recommended processing scheme.